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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : H01M 12/06

A1

(11) International Publication Number: WO 00/33411

(43) International Publication Date: 8 June 2000 (08.06.00)

(21) International Application Number: PCT/US99/28120

(22) International Filing Date: 30 November 1999 (30.11.99)

(30) Priority Data:

09/201,524	30 November 1998 (30.11.98)	US
60/112,292	15 December 1998 (15.12.98)	US
60/129,502	15 April 1999 (15.04.99)	US

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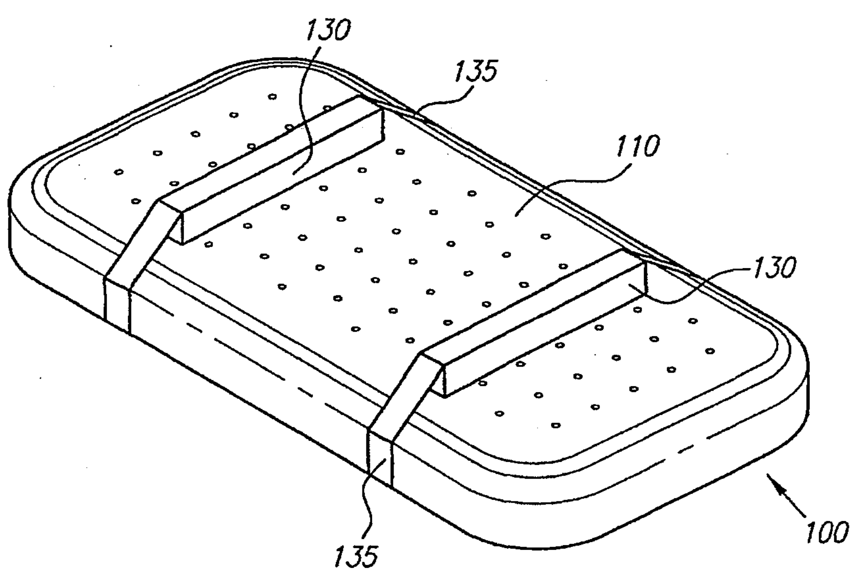
(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PRESSURIZED METAL-AIR BATTERY CELLS



(57) Abstract

Applying pressure to metal-air battery cells (such as zinc-air battery cells) results in a significant drop in the voltage delay effect. In addition, applying pressure to these cells also increases the output voltage. Pressure may be applied to the outside of the cell housing, or by pressurizing the internal contents of the cell.

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SPECIFICATION

TITLE

PRESSURIZED METAL-AIR BATTERY CELLS

CROSS REFERENCE TO RELATED APPLICATIONS

Priority is claimed to U.S. application No. 09/201,524, filed on November 30, 1998; U.S. application No. 60/112,292, filed on December 15 1998; and U.S. application No. 60/129,502, filed on April 15, 1999, and each of these applications is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

The present invention relates to alkaline electrochemical cells, particularly to metal-air cells. Even more particularly, the invention relates to such cells in low temperature and low humidity environments. Still more particularly, the invention relates to the application of pressure to such cells to improve low temperature and low humidity performance, particularly, the voltage delay phenomenon.

BACKGROUND OF THE INVENTION

New battery technologies have emerged that have, in principle at least, the ability to power high-drain electrical devices by generating a sufficient amount of energy and power at a sufficiently low cost. One such technology is alkaline batteries which have demonstrated very high energy to mass ratios. A particular kind of alkaline battery, metal-air batteries, in particular, has the potential for extremely high energy to weight ratios. A zinc-air battery utilizes ambient oxygen as one of its electrode, thereby allowing all the space for electrodes to be used to store the single metal electrode and electrolyte. Because the cell needs to house only the metal electrode (and electrolyte), and the other electrode cannot run out, tremendous space-utilization efficiencies may be realized. First, the metal electrode can be totally consumed since there is no complementary electrode that is at risk of running out first. Second, very little internal volume is required to provide for the complementary electrode. As a result, the energy to volume (or mass) ratio of metal-air cells is very high.

One problem associated with alkaline batteries is that their performance is adversely affected by exposure to cold temperatures. In one type of alkaline battery, metal-air cells, the performance is adversely affected by low humidity environments due to the escape of

moisture from the cell's air holes. Exposure to cold temperatures slows the electrochemical reactions of the battery cell, which can have a similar effect. These ambient conditions cause, in effect, premature aging of the battery by causing the voltage to drop, early in the discharge history of the cell, to a level below the minimum required for the proper operation of battery powered device.

One adverse consequence of exposure to low temperatures is voltage delay. This problem is characterized by an immediate voltage drop at the instant increased current is demanded, such as after a period when the battery-powered device is turned off or before the battery's first use. After a few minutes, the voltage of the battery cell increases and then stabilizes.

SUMMARY OF THE INVENTION

The invention provides an alkaline battery cell capable of increased performance by providing external pressure on the cell. The effect is appreciable in low humidity conditions where air cells tend to dry out. However, enhanced performance and tolerance of low-humidity provides a benefit to regular alkaline cells as well as metal-air cells, because the external pressure permits the use of a higher ratio of electrode material to electrolyte, thereby extending the cell's power capacity.

To utilize the invention, a battery cell may be designed to apply external pressure to elevate the pressure within the battery cell. This produces the unexpected result of increasing the metal-air battery cell's performance in room and cold temperature environments. Elevated pressure can be applied to the materials involved in the metal-air electrochemical process by various mechanisms. Pressure can be created, for example, by the use of indentations in the battery cell after the cell is manufactured. Alternatively, it can be generated by the use of tightened straps that surround the battery cell, springs or parallel plates that compress the battery cell, or by other external pressure sources on the battery cell. Alternatively, pressure is created in the battery cell during construction of the battery cell, such that the battery cell casing elements apply pressure to the battery cell's contents.

Alkaline cells can expand due to accumulation of hydrogen gas resulting from parasitic oxidation of the metal electrode or expansion due to the metal transforming to its oxide. Such increases in pressure can cause a rupture or leak. In addition to providing a mechanism for increasing pressure within the battery cell, indentations or other housing features can be shaped to deform progressively when pressure from the cell gets too high so

that a constant internal pressure can be maintained. This helps to prevent the battery cell from failing or leaking due to uncontrolled expansion. The deformation provided by an indentation can be designed so that it either progressively collapses under an over-pressure condition or undergoes paroxysmal collapse to protect the cell from rupture. The progressive collapse (or reversal) of the indentation has the advantage of permitting a constant pressure to be maintained despite progressive expansion of the cell during discharge due to zinc oxide formation.

To alleviate the problem due to the inevitable expansion of alkaline battery cells, the battery cell can be made flexible and/or strong enough to accommodate the increased pressure. A venting system can alternatively be added to help maintain optimum pressure within the battery cell by permitting release of hydrogen gas.

While the invention will now be described in connection with certain preferred embodiments and in reference to the appended figures, it is not intended to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications, and equivalents as may be included within the scope of the invention. Thus, the following description and examples of the preferred embodiments of the invention are only intended to serve to illustrate the practice of the present invention, it being expressly understood that the particulars shown are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description taken with the drawings making it apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a perspective view of a prismatic metal-air battery cell.

FIG. 1B is a section view of the embodiment of FIG. 1A.

FIG. 2 is a perspective view of a prismatic metal-air battery cell with external straps and blocks.

FIG. 3A is a side view of the prismatic metal-air battery cell with indentations.

FIG. 3B is a top view of a prismatic metal-air battery cell with indentations.

FIG. 3C is a top view of a prismatic metal-air battery cell with indentations.

FIG. 3D is a cross-sectional view of the prismatic metal-air battery cell shown in FIG. 3C.

FIG. 3E is a side view of a prismatic metal-air battery cell with indentations along the battery cell side walls.

FIG. 3F is a side view of a prismatic metal-air battery cell with parallel plates compressing the battery cell.

FIG. 3G is a top view of a prismatic metal-air battery cell with parallel plates compressing the battery cell.

FIG. 4 is a partial cross-sectional view of a prismatic metal-air battery cell with expandable foam.

FIG. 5 is a cross-sectional view of an alternative embodiment of the invention. The embodiment utilizes a snap-fitting strap to increase pressure within the battery cell.

FIGS. 6 and 7 show typical curves demonstrating the voltage delay phenomena.

FIGS. 8 and 9 show the effect of pressure on battery cell voltage and voltage delay.

FIGS. 10 and 11 show the effect of pressure on battery cell voltage, recovery rate and voltage delay.

FIGS. 12-14 show the effect of pressure on voltage delay.

FIGS. 15 and 16 show the effect of pressure at 30% discharge after three days storage at 20% relative humidity.

FIG. 17 shows typical discharge curves of pressurized and unpressurized battery cells at low temperature.

FIG. 18 shows the discharge curves of battery cells subject to a range of external pressure.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

As previously noted and described *infra*, it has been found that performance is substantially ameliorated by the application of pressure to the contents of battery cells. Pressurized battery cells provide substantially higher voltages over their discharge history than unpressurized battery cells. Pressure also reduces the voltage delay phenomenon. This problem is characterized by a voltage drop immediately after a long period of open circuit voltage condition or during the use of a new battery cell. Pressure also improves the performance of battery cells, particularly metal-air cells used in low humidity environments.

Referring to FIGS. 1A and 1B, performance increases due to pressure were experimentally observed on prism-shaped zinc-air cells (see examples 1-3, *infra*). A prism-

shaped zinc-air cell 100 has a generally planar elements including an outer casing element 125 on a cathode side 100A of the cell 100, a diffuser 20, air cathode active layer 45, separator 55, anode 30, and outer casing element 141 on the anode side 100B of the battery cell 100. Air gases diffuse into and out of the cell through holes 50 in the casing. The internal layers of the battery cell 100, including diffuser 20, air cathode 45, separator 55, and anode 30, are all sandwiched between the outer casing elements 125 and 141. The anode includes finely divided metal (e.g., zinc powder) in a slurry formed with potassium hydroxide and a gelling agent as described below. The outer casing elements are substantially rectangular with each having a major surface 110 and 140. The outer casing elements can be constructed from either metal or plastic.

As a result of these findings, one aspect of the present invention is to create and control pressure within battery cells. While the application of pressure to prismatic shaped metal-air battery cells is described below, the invention can be used in all types of battery cells, including alkaline battery cells.

In one embodiment, as shown in FIG. 2, pressure is applied by wrapping the battery cell 100 with external straps 135. After the metal-air battery cell 100 construction is completed, straps 135 are placed around the battery cell 100 over pressure blocks 130. The straps 135 are tightened and the blocks 130 compress the major surface 110 of the cathode casing element, creating pressure within the battery cell 100. Alternatively, the blocks 130 can be placed so as to compress the major surface of the anode casing element (not shown).

In an additional embodiment, as shown in FIGS. 3A and 3B, indentations 145 are created on the major surface 140 of the anode casing element 141 to create pressure within the battery cell 100. These indentations 145 increase pressure within the battery cell 100, as well as making the major surface 140 of the anode casing element 141 more ridged and less susceptible to deformation under pressure. The indentations 145 can be placed vertically along the width or length of the major surface 140 of the anode casing element 141, or diagonally across this major surface 140. Moreover, the indentations can alternatively be located on the major surface 110 of the cathode casing element 125.

Although pressure has been found to increase the battery cell's 100 performance, if the pressure reaches too high a level (due to zinc oxide and hydrogen formation), the battery cell 100 may leak or fail due to uncontrolled expansion. This is especially true with plastic metal-air battery cells due to the weaker bonds that hold the battery cell outer casing elements together (metal casing elements are inherently mechanically stronger as are the bonds

between the two halves of metal cells). The indentations described in the listed embodiments not only increase the battery cell's performance, but also provide avenues for controlled expansion of the battery cells 100. Minimizing battery cell 100 failure due to increased pressure.

Alternative embodiments showing the use of indentations are illustrated in FIGS. 3C, 3D, 3E, 3F and 3G. FIGS. 3C and 3D show indentations 150 punched at several places across the major surface 140 of the anode casing element 141. Additionally, the major surface of the cathode casing element (not shown) can be indented in this manner.

FIG. 3E shows indentations 155 on the side walls 156 of the battery cell 100. These indentations 155 can be located along the length and/or width of the battery cell 100.

In an additional embodiment, as shown in FIGS. 3F and 3G, two plates 165 are used to sandwiched the battery cell 100. Straps 170, or some other fastening means such as screws, compress the plates 165 into the battery cell 100 generating pressure within the battery cell 100. Although not shown in the drawings, cutouts are made in the plate on the cathode side of the battery cell. This ensures that air is supplied to the air access holes in the battery cell.

Pressure can also be generated during construction of the battery cell 100. This pressure allows the battery cell casing elements to apply pressure to the battery cell's 100 contents. The battery cell casing elements can be crimped or otherwise attached so as to create this pressure.

Additionally, the expansion of the battery cell 100 due to zinc oxide formation can create and maintain pressure within the battery cell 100. As the volume of the zinc anode/oxide increases within the battery cell 100, the battery cell outer casing elements apply pressure to the battery cell's 100 contents. To ensure that pressure does not rise above a certain level, the battery cell casing elements may be formed in such a way as to yield at a certain pressure, allowing continued expansion. Alternatively, expandable foam can be used in combination with a pressure control mechanism in the battery cell 100. Such a mechanism could include a vent or valve to relieve pressure above a certain amount).

Woodruff et al., United States Patent No. 5,328,778 ('778), describes the use of expandable foam and a vent opening to minimize pressure buildup. As shown in FIG. 4, expandable foam 175 can be used in the present invention to maintain a given pressure within the battery cell 100. The foam 175 is placed between the anode material 176 and the major surface 140 of the anode casing element 141. The expandable foam 175 is selected so as to

maintain a set elevated pressure in the battery cell 100. The foam 175 is designed to collapse at a set pressure, while a valve or vent (not shown - e.g., a pressure valve) is inserted to ensure that the pressure in the battery cell 100 does not rise above a certain pressure.

Referring now to FIG. 5, in an alternative embodiment, a strap 180 is wrapped tightly around the cell 100 to elevate the pressure within the battery cell 100, while also resisting the deformation and the bulging of the battery cell 100. The strap 180 is snap fitted onto the battery cell 100. It is preferred that the strap 180 be made of an insulated and resilient material so that the strap 180 does not cause the battery cell 100 to short circuit. Although not illustrated here, the outer casing elements can contain recesses shaped to fit the strap 180 so that the strap 180 is at least partially embedded in the cathode and/or anode casing elements. Depending on the configuration of the battery cell 100, the strap 180 can also assist in the attachment of the battery cell outer casing elements.

The following examples are descriptions of the use of the present invention. These examples are not meant to limit the scope of the invention, but are merely embodiments.

EXAMPLE 1

Voltage delay is characterized by a voltage drop immediately after current is applied, usually after a long period in open circuit voltage condition or after the battery cell's construction (fresh battery cell). The battery cell voltage then recovers within a few minutes and stabilizes. This problem is caused mainly at the air electrode and separator side of the battery cell, probably as a result of water evaporation and/or by electrolyte rejection. External pressure has been found to decrease the voltage delay and increase the battery cell voltage.

In order to understand and to solve this problem, the effect of pressure on voltage delay was investigated in both metal and standard plastic metal-air battery cells. All the battery cells were discharged in GSM regime for 10% or 20% discharge every two days at open circuit voltage (50% relative humidity and room temperature). The battery cells were pressurized with the use of a "Jig" having two plates acting as a vise with four screws to compress cells between the plates.

The anode mixture was prepared as follows:

1. 560 g thermal zinc powder (Mitsui Mining & Smelting Co. Ltd., ABI grade) was mixed with 5 g Carbopol 941 (B. F. Goodrich), a polyacrylic acid gelling agent, to form a uniform mixture;
2. 435 g of an aqueous deionized (DI) water solution of 8.5 M KOH (Oxychem Co.), 22g/L in zincates, was added to the zinc/Carbopol mixture and mixed to obtain a uniform blend.

The zincates were first prepared by adding 27.4 g ZnO (Durcam, Electrolux grade) to a liter of DI water, 8.5 M in KOH; and

3. The blend was allowed to sit for 24 hours before dosing.

The dosed blend contained 56.0:0.5:43.5 % (w/w %) of zinc powder, Carbopol and KOH solution, respectively. Each cell contained 5.6 g of this blend.

The cathode was prepared as follows:

1. 240 g of MnO_2 (Aldrich Chemical Company, Milwaukee WI) was ground in a mill for 24 hours to a fine powder, poured into two liters of deionized (DI) water and then heated to 85°C. While stirring, 800 g of Darco G-60 carbon (American Norit, Atlanta GA) was added. This was followed by adding 288 cc of DuPont 30-N PTFE suspension. The suspension/mixture was stirred for one hour, after which the active mass was filtered and dried at 120°C for 5 hours;

2. 200 g of the dry active mass was slowly added to five liters of DI water. This mass was stirred and heated at 85°C until dry;

3. The active mass was then spread evenly over a nickel mesh (40 X 40 mesh, 0.005 mm diameter nickel from National Standard) and pressed to form the active layer of the electrode. A porous PTFE sheet was then pressed on to one side of the active layer;

4. The air electrode was then laminated with a non-woven separator and a microporous polypropylene film (grade 3501 from Celgard®) on the side distal from the PTFE sheet. The lamination was effected using PVA (polyvinyl alcohol from Aldrich Chemical) as a glue; and

5. The air electrode was placed inside the cell's cathode casing and the casing filled with the zinc gel prepared above. The anode casing was placed above the cathode casing. When metal casings were used, the cell was closed by crimping the cathode casing to the anode casing with a nylon grommet positioned between them to prevent electrical shorting. When the cells were made of plastic, the cell was closed by gluing the casings together. The plastic cell also contained a nickel wire mesh current collector for the zinc anode which can be omitted from metal cells.

All cells were discharged according to a GSM (Global Systems Mobile) profile. The GSM profile consisted of repetitive cycles of 1.34 A for 0.5 millisecond followed by 0.078 A for 4.1 milliseconds for the duration of the discharge. The discharge was carried out in increments of 10 or 20% depth of discharge (DOD) every two days. Between discharges, the cells were stored at open circuit voltage (OCV), at 50% relative humidity (RH) and at room temperature (RT). The discharges were measured using a Maccor 4000 Gen 4 Battery Tester.

Impedance was measured at 1 kHz with a Hewlett-Packard milli-ohmeter. Temperature and humidity were controlled using a Thermatron 2800 Environmental Chamber.

The cells were pressed between the metal plates of a jig with a plastic insulating layer between the plates and the cells. Pressure was controlled using screws connecting the plates to the jig. The force applied was generally between 39.2-58.8 N equivalent to a pressure of about 03.4-5.2 N/cm^2.

Metal battery cells

A typical curve of voltage delay phenomena is shown in FIG. 6. It can be seen that when current is applied, the battery cell voltage drops and reaches a minimum after about six seconds (see FIG. 7). The battery cell's voltage then recovers and stabilizes. The results are summarized in table 1. V_{min} caused by the delay and V_{max} the maximum voltage following recovery and stabilization of the voltage.

Table 1- Voltage delay as function of depth of discharge for unpressed metal cells

	y2532		y2529	
% discharge	V_{min} [V]	V_{max} [V]	V_{min} [V]	V_{max} [V]
0	1.035	1.07	1.06	1.095
10	1.005	1.045	1.025	1.06
20	1.01	1.05	1.025	1.06
30[1]	1.00	1.05	1.02	1.065
50	1.035	1.075	1.00	1.08
70	1.04	1.065	1.05	1.075

1 - After three days at open circuit voltage

From this table it can be seen that the lowest minimum voltage is observed between 20%-40% discharge. The values of the voltage delay were about 35 mV at 0-20% discharge. The maximum voltage delay values were about 70 mV between 20%-40% discharge. This value decreased after 40% discharge to 25 mV at 70% discharge. Table 1 shows that the voltage never dropped below 0.9 V, the minimum acceptable voltage for cells intended for a cellular phone battery pack. The voltage delay was about 35 mV at 0 - 20% discharge. The maximum voltage delay was about 70 mV which occurred between 20 - 40% discharge. This maximum decreased to 25 mV at 70% discharge.

Effect of pressure

FIGS. 8 and 9 show the effect of pressure on battery cell voltage and voltage delay. It can be seen that the shape of the curve is similar in both pressurized and unpressurized metal-

air battery cells. However, the battery cell voltage was higher for the pressed cell and the voltage delay lower compared to the unpressed cell. In addition, it can be seen that the recovery rate of the voltage in pressurized battery cells is faster. The results of the effect of pressure on battery cell voltage and voltage delay are summarized in table 2.

Table 2 - Voltage delay as a function of depth of discharge for pressed metal cells

	y2539		y2536	
%discharge	V_{min} [V]	V_{max} [V]	V_{min} [V]	V_{max} [V]
0	1.065	1.08	1.07	1.105
10	Leaked[2]		1.04	1.07
20[1]			1.055	1.08
30			1.06	1.085
50			1.065	1.08
70[1]			1.06	1.08

1 - After three days at open circuit voltage
2 - Leaking through the casing holes as a result of a seal damage. No polytetrafluoroethylene (PTFE) delamination was observed.

From this table it can be seen that one battery cell failed because of leaking problems. However, a very low value of voltage delay was observed (15 mV). In addition, smaller values of voltage delay were obtained in the other battery cell (compared to the unpressurized battery cells). The maximum voltage delay was 35 mV at 0% discharge. This value decreased with percentage discharge down to 15-20 mV. The lowest V_{min} value was obtained at 10% discharge.

To further analyze the effect of pressure, a cell containing smaller zinc particles (<250 microns) and 0.3% Carbopol (941) was analyzed. All other experiments in this and the other examples of this application were carried out using zinc powder with a particle size distribution of approximately 50-500 microns. The unpressed cell was first discharged to 30 % DOD. The cell was then kept for a day at OCV, 50% RH and RT. The unpressed cell was discharged for a short 15 minute period thereby not significantly reducing total electrical capacity. The cell was then kept for another day at OCV, 50% RH and RT, pressed and discharged for another 15 minutes period. As can be seen from Figs 10 and 11, pressure induces a higher cell voltage, faster recovery rate and lower voltage delay. It appears that particle size and Carbopol concentration do not affect the general pressure/voltage delay relationship.

Unpressed plastic cells

In general, the voltage delay curves of plastic and metal cells are similar. However, much larger voltage delays are observed in plastic cells. Table 3 summarizes the results of the discharge of an unpressed plastic cell.

Table 3 - Voltage delay as a function of depth of discharge for unpressed plastic cell

	Cell # - B284	
% Discharge	Vmin[V]	Vmax[V]
0	1.055	1.08
10	0.81	1.05
20	0.945	1.055
30[1]	0.96	1.05
50[2]	1.025	1.03
70	0.99	0.99

[1] - After three days at OCV.
[2] - After ten days at OCV.

It can be seen that the lowest voltage of V_{min} was obtained at 10% discharge. This value was lower than 0.9 V, which is a practical lower limit for certain applications, for example, cellular phone applications. The maximum voltage delay was 240 mV which occurred at 10% depth of discharge.

Plastic battery cells - pressurized

To analyze the effect of pressure on cell impedance, the impedance of fresh plastic cells was measured at 1 kHz. Table 4 summarizes the results.

Table 4 - Effect of pressure on impedance

Cell #	Impedance (Z) @ 1 kHz for unpressed cell [ohm]	Impedance (Z) @ 1 kHz for pressed cell [ohm]
B280	0.12	0.10
B282	0.12	0.09

As in metal cells, the shape of the voltage delay curves of pressed and unpressed plastic cells are similar. Again as in metal cells, cell voltage increases and voltage delay decreases with the application of pressure (Fig. 12-14). The results of the pressed plastic cells are summarized in Table 5.

<u>Table 5 -</u> Voltage delay for pressed plastic cells

	Cell # - B282		Cell # - B280	
% discharge	Vmin [V]	Vmax [V]	Vmin [V]	Vmax [V]
0	1.1	1.12	1.02	1.095
10	0.96	1.05	0.95	1.04

It can be seen that pressed plastic cells exhibited very small voltage delays compared to unpressed plastic cells. These values are about 50% smaller than comparable values in unpressed cells. The lowest value of V_{min} was obtained at 10% discharge, but even this value exceeds the minimum acceptable value of 0.9 V.

It is believed the voltage delay problem is caused by water evaporation and/or electrolyte rejection from the air electrode and separator side. The fact that the battery cell voltage reaches a minimum after about six seconds suggests that the voltage delay problem is not only an IR (voltage) problem but also a diffusion problem (probably water diffusion).

It appears that after 50% discharge this problem becomes insignificant. This is probably due to zinc oxide and hydroxide precipitation having a higher molar volume (about triple) than zinc. The volume occupied by these solids increases with percentage discharge, pushing the electrolyte towards the air electrode and the voltage delay is reduced.

It also appears that the voltage delay values are reduced (about 50% lower when the voltage delay values reaching maximum) and the battery cell voltage is increased (about 20 mV in metal battery cells and by 40 mV in plastic battery cells) in both metal and plastic battery cells as a result of external pressure. External pressure reduces the battery cell volume and might cause the same effect as zinc oxide and hydroxide precipitation. This improvement is related to the improvement in impedance, better contact of the air electrode and the separator and to the shorter path that water has to pass through to reach and wet the air electrode and separator.

In most cases the voltage delay value reaches a maximum between 10%-30% discharge. This can be related to the voltage dip caused by the zinc electrode. From the literature, the impedance rises by about 20% at the stage when the dip voltage is reaching minimum. In CB this dip reaching minimum typically at 20% discharge. It can be concluded that this dip voltage delay is obtained at 10% discharge. It can be concluded that this dip is "moved" to an early discharge stage by external pressure.

The voltage delay in plastic battery cells is much higher than in metal battery cells.

EXAMPLE 2

Metal cells in this example were prepared as described in Example 1. Except where otherwise noted, the methods and procedures used in Example 1 were also applied here. The purpose of these experiments was to determine the effect of pressure on cells kept at low relative humidities.

Four battery cells were discharged 20%. After three days at open circuit voltage at 20% relative humidity, two of them were pressurized. Then, the four battery cells were discharged at GSM regime at 30% discharge.

After three more days at open circuit voltage at 20% relative humidity, the two pressurized battery cells were further pressurized. The four battery cells were discharged one hour at GSM regime. In addition, the impedance at 1 kHz was measured at different stages of the battery cells. The results are summarized in tables 6 and 7.

Table 6: The effect of pressure at 20% discharge

Battery cell no.	1 kHz in fresh battery cells [ohm]	1 kHz at 20% discharge [ohm]	1 kHz at 20% discharge (after three days at storage) [ohm]	1 kHz at 20% discharge and three days at storage (after pressure) [ohm]	V_{min} [mV]	V_{max} [mV]
4957	0.12	0.2	0.21		910	1010
4950	0.11	0.2	0.15		925	1020
4938	0.13	0.22	0.2	0.15	955	1025
4935	0.11	0.17	0.13	0.1	980	1040

From table 6 it can be seen that: (1) in pressurized battery cells the value of V_{min} is 50 mV higher than in unpressurized battery cells; (2) in pressurized battery cells the value of V_{max} is 20 mV higher than in unpressurized battery cells; (3) the battery cells impedance is improved by about 25% by applying some pressure; (4) the rate of voltage recovery is improved in pressurized battery cells (see FIGS. 15 and 16); and (5) at 20% discharge the impedance is increased by about 70% compared to fresh battery cells (the bottom of the dip).

Table 7: The effect of pressure at 30% discharge

Battery cell no.	1 kHz at 30% discharge (after three days at storage) [ohm]	1 kHz at 30% discharge and three days at storage (after harder pressure) [ohm]	V_{min} [mV]	V_{max} [mV]
4957	0.21		865	1000
4940	0.2		900	1040
4938	0.17	0.15	945	1030
4935	0.14	0.13	990	1050

From table 7 it can be seen that: (1) in pressurized battery cells the difference between V_{min} and V_{max} is 70 mV lower than in unpressurized battery cells (about 50% lower - 70 mV in pressurized battery cells and 140 mV in unpressurized battery cells); (2) in pressurized battery cells the value of V_{min} is 85 mV higher than in unpressurized battery cells; (3) in unpressurized battery cells the value of V_{min} is 900 mV and lower; (4) the impedance is not improved significantly after applying higher pressure; and (5) the rate of voltage recovery is improved in pressurized battery cells (see FIGS. 15 and 16).

EXAMPLE 3

Metal cells in this example were prepared as described in Example 1. Except where otherwise noted, the methods and procedures used in Example 1 were also applied here. The purpose of these experiment was to determine the effect of pressure on cells kept at low temperature and after storage.

The effect of pressure at 0°C

The effect of pressure was tested at 0°C in GSM regime. FIG. 17 shows typical discharge curves of pressurized and unpressurized battery cells. It can be seen that at the beginning of discharge there is no difference between the two curves; however, after 1.5 hours the voltage of the pressurized battery cell starts to rise and is maintained at 890 mV, whereas the voltage of the unpressurized battery cell decreases further and stabilized at 820 mV. Additionally, it appears that there is no difference in the cells' capacity (1.7 Ah) between pressed and unpressed cells.

Another experiment was conducted to be sure that the effect described is not the effect of heating. This time four battery cells were assembled inside the Jig, two battery cells were pressurized and two battery cells were unpressurized. The results are summarized in Table 8.

Table 8

Battery cell	Condition	Capacity to 0.5V cutoff [Ah]	Plateau voltage [V]
y5191	Pressurized	1.8	0.88
y5195	Pressurized	1.5	0.85
y5194	Unpressurized	1.5	0.81
y5204	Unpressurized	1.7	080

From this table it can be seen that only in pressurized battery cells the voltage was increased. Thus, it can be concluded that the voltage increase is not an effect of heating.

To check that this effect is a pressure effect, two unpressed battery cells were discharged at 0°C inside a Jig. After three hours the battery cells were pressed and discharged for two hours. After two hours discharge, the pressure was released and the battery cells were discharged for another two hours. FIG. 18 shows the discharge curves of these battery cells at 0°C, GSM. It can be seen that when no pressure was applied, the voltage was maintained at about 940 mV when there is a slightly difference between the battery cells voltage. This relatively high voltage is caused probably as a result of a change in battery cells - contains 5.9 g gel instead of 5.5 g.

After pressure was applied, the voltage starts to rise and maintained at 970 mV. The fact that the change in voltage takes time suggests that the voltage changes mainly due to a mass transport process. It can also be seen that there is no difference in the battery cell voltage. This suggests that the pressure might improve the reproducibility in battery cell production and performance.

After pressure was released, the battery cell voltage decreased and maintained at about 900 mV. In addition, a difference in the battery cell voltage can be observed.

The effect of pressure at room temperature

The effect of pressure was tested at room temperature. From the discharge results, the only change observed is that the capacity of the pressurized battery cells was 4% lower (2.4 Ah for pressurized battery cells and 2.5 Ah for unpressurized battery cells - table 9).

Table 9

Battery cell	Condition	Capacity to 0.9V [Ah]
y5779	Pressurized	2.4

y5793	Pressurized	2.4
	Unpressurized	2.5

The effect of pressure in storage (seven days at room temperature at 50% relative humidity) was also tested. Four battery cells were tested, two of them were pressurized prior to storage and discharged under pressure. Discharge results showed that there was no difference in the battery cell voltage or in their capacity (see table 10).

Table 10

Battery cell	Condition	Capacity to 0.9V [Ah]
y5184	Pressurized	2.3
y5192	Pressurized	2.5
y5186	Unpressurized	2.5
y5186	Unpressurized	2.3

To test the effect of pressure on the battery cell impedance at 1 kHz, the impedance of the battery cells were measured. It appears than when pressure was applied, the impedance dropped by 20% (usually from 0.12 to 0.1 ohm). When the pressure was released, the impedance rose to its initial value (see table 11).

Table 11

Battery cell	Impedance at 1 kHz [ohm]		
	Press. off	Press. on	Press. off
y5182	0.12	0.1	0.12
y5189	0.12	0.1	0.12

Although the invention has been described with reference to preferred embodiments and specific examples, it will readily be appreciated by those of ordinary skill in the art that many modifications and adaptations of the invention are possible without departure from the spirit and scope of the invention.

What is claimed is:

1. A method of minimizing voltage delay in a metal-air battery cell, comprising the step of pressurizing the cell above atmospheric pressure.

2. The method of claim 1, wherein the metal-air battery cell is a zinc-air battery cell.

3. The method of claim 1, wherein, the cell is pressurized to between about 3.4 and about 5.2 N/cm^2 above atmospheric pressure.

4. A method of increasing an output voltage of a metal-air battery cell, comprising the step of pressurizing the cell above atmospheric pressure.

5. The method of claim 4, wherein the metal-air battery cell is a zinc-air battery cell.

6. The method of claim 4, wherein, the cell is pressurized to between about 3.4 and about 5.2 N/cm^2 above atmospheric pressure.

7. A method of minimizing voltage delay in a metal-air battery cell, comprising the step of pressing a portion of a wall of the cell inward to form an indentation that increases an internal pressure of the cell above atmospheric pressure.

8. The method of claim 7, wherein the metal-air battery cell is a zinc-air battery cell.

9. The method of claim 8, wherein, the internal pressure in the cell is increased to between about 3.4 and about 5.2 N/cm^2 above atmospheric pressure.

10. The method of claim 8, wherein the indentation is channel-shaped.

11. The method of claim 8, wherein the indentation is round.

12. The method of claim 8, wherein the indentation is formed so that when the pressure inside the cell exceeds a threshold, the indentation will deform in an outward direction, so as to reduce the pressure inside the cell.

13. The method of claim 8, wherein the indentation is formed so that when the pressure inside the cell exceeds a threshold, the indentation will undergo a first deformation in an outward direction, so as to reduce the pressure inside the cell, and wherein, if the pressure exceeds a second threshold after the first deformation has occurred, the indentation will undergo a second deformation in an outward direction so as to reduce the pressure inside the cell a second time.

14. The method of claim 8, wherein the indentation undergoes progressive outward deformation as the pressure inside the cell increases beyond a threshold.

15. The method of claim 8, further comprising the step of pressing at least one additional portion of the cell wall inward to form at least one additional indentation.

16. The method of claim 8, further comprising the step of pressing at least one portion of a second cell wall inward to form at least one additional indentation.

17. A method of minimizing voltage delay in a metal-air battery cell, comprising the steps of:

sealing contents of the cell into the cell;

building pressure up within the cell to above atmospheric pressure by allowing hydrogen gas to accumulate in the cell; and

ensuring that the pressure inside the cell does not build up beyond a threshold.

18. The method of claim 17, wherein the metal-air battery cell is a zinc-air battery cell.

19. The method of claim 18, wherein, in the building step, the pressure is built up to to between about 3.4 and about 5.2 N/cm^2 above atmospheric pressure.

20. The method of claim 18, wherein the ensuring step includes the step of venting the hydrogen gas when the pressure inside the cell exceeds the threshold.

21. The method of claim 18, wherein the ensuring step includes the step of including, within the cell, a material that collapses under pressure so that when the internal pressure of the cell exceeds the threshold, the collapse of the material will reduce the pressure in the cell.

22. A method of minimizing voltage delay in a metal-air battery cell, comprising the steps of pressurizing the cell by squeezing contents of the cell when the cell is crimped together during assembly of the cell.

23. The method of claim 22, wherein the metal-air battery cell is a zinc-air battery cell.

24. The method of claim 23, further comprising the step of ensuring that the pressure inside the cell does not build up beyond a threshold by venting the cell when the pressure inside the cell exceeds the threshold.

25. The method of claim 23, further comprising the step of ensuring that the pressure inside the cell does not build up beyond a threshold by including, within the cell, a material that collapses under pressure so that when the internal pressure of the cell exceeds the threshold, the collapse of the material will reduce the pressure in the cell.

26. A method of minimizing voltage delay in a metal-air battery cell, comprising the step of sealing contents of the cell into the cell in an environment having a pressure above atmospheric pressure.

27. The method of claim 26, wherein the metal-air battery cell is a zinc-air battery cell.

28. The method of claim 27, wherein, the cell is sealed in an environment in which the pressure is between about 3.4 and about 5.2 N/cm^2 above atmospheric pressure.

29. The method of claim 27, further comprising the step of ensuring that the pressure inside the cell does not build up beyond a threshold by

venting the cell when the pressure inside the cell exceeds the threshold.

30. The method of claim 27, further comprising the step of ensuring that the pressure inside the cell does not build up beyond a threshold by including, within the cell, a material that collapses under pressure so that when the internal pressure of the cell exceeds the threshold, the collapse of the material will reduce the pressure in the cell.

31. A method of minimizing voltage delay in a metal-air battery cell, comprising the step of applying external pressure to the cell.

32. The method of claim 31, wherein the metal-air battery cell is a zinc-air battery cell.

33. The method of claim 32, wherein the external pressure applied in the applying step is between about 3.4 and about 5.2 N/cm^2 above atmospheric pressure.

34. The method of claim 32, wherein the step of applying external pressure to the cell includes the step of pressing a first wall of the cell towards a second wall of the cell.

35. The method of claim 32, wherein the step of applying external pressure to the cell includes the step of tightening a strap around the cell.

36. The method of claim 32, wherein the step of applying external pressure to the cell includes the step of tightening an insulating strap around the cell.

37. The method of claim 32, wherein the step of applying external pressure to the cell includes the steps of placing blocks against the cell, and tightening a strap around the blocks.

38. The method of claim 37, wherein the blocks have air holes arranged to allow air to reach air holes on the battery cell.

39. The method of claim 32, wherein the step of applying external pressure to the cell includes the steps of placing blocks against the cell, and urging the blocks together using a spring.

40. The method of claim 39, wherein the blocks have air holes arranged to allow air to reach air holes on the battery cell.

41. The method of claim 32, wherein the step of applying external pressure to the cell includes the step of placing the cell on top of a surface, and placing a heavy object on top of the cell.

42. The method of claim 32, wherein the step of applying external pressure to the cell includes the step of placing the cell between two blocks, and urging the blocks together using at least one screw.

43. The method of claim 42, wherein the blocks have air holes arranged to allow air to reach air holes on the battery cell.

44. A metal-air battery cell comprising:

a case having a wall, the wall having an indentation;

an air electrode enclosed within the case;

a first terminal electrically connected to the air electrode;

an anode mixture including an electrolyte and metal particles;

a second terminal electrically connected to the mixture; and

a separator located between the air electrode and the anode mixture, in physical contact with the air electrode and with the anode mixture, said separator being of such material as to permit ions to travel between the air electrode and the anode mixture and to block metal particles from contacting the air electrode.

45. The metal-air battery of claim 44, wherein the metal particles include zinc particles.

46. The metal-air battery of claim 44, wherein the indentation is channel-shaped.

47. The metal-air battery of claim 44, wherein the indentation is round.

48. The metal-air battery of claim 44, wherein, when the pressure inside the cell exceeds a threshold, the indentation deforms in an outward direction, so as to reduce the pressure inside the cell.

49. The metal-air battery of claim 44, wherein, when the pressure inside the cell exceeds a threshold, the indentation undergoes a first deformation in an outward direction, so as to reduce the pressure inside the cell, and wherein, when the pressure exceeds a second threshold after the first deformation has occurred, the indentation undergoes a second deformation in an outward direction so as to reduce the pressure inside the cell a second time.

50. The metal-air battery of claim 44, wherein the indentation undergoes progressive outward deformation as the pressure inside the cell increases beyond a threshold.

51. The metal-air battery of claim 44, further comprising at least one additional indentation in the cell wall.

52. The metal-air battery of claim 44, wherein the cell has a second wall, and the second wall has at least one indentation.

53. An apparatus comprising:

a metal-air battery cell having a housing, the housing having a first wall and a second wall opposite to the first wall;

a first block located adjacent to and pressed against the first wall, the first block shaped to conform substantially to a shape of the first wall; and

a second block located adjacent to and pressed against the second wall, the second block shaped to conform substantially to a shape of the second wall.

54. The apparatus of claim 54, wherein the metal-air battery cell is a zinc-air battery cell.

55. The apparatus of claim 55, wherein the cell housing is plastic.

56. The apparatus of claim 55, wherein the cell housing is metal.

57. The apparatus of claim 55, wherein the first block is pressed against the first wall and the second block is pressed against the second wall with a pressure of between about 3.4 and about 5.2 N/cm^2 above atmospheric pressure.

58. The apparatus of claim 55, wherein the blocks are pressed against the walls by at least one spring.

59. The apparatus of claim 55, wherein the blocks are pressed against the walls by elastic.

60. The apparatus of claim 55, wherein the blocks are pressed against the walls by gravity.

61. The apparatus of claim 55, wherein the blocks are pressed against the walls by screw action.

62. The apparatus of claim 55, wherein the blocks are pressed against the walls by hydraulic action.

63. The apparatus of claim 55, wherein the battery cell has air holes, and the first and second blocks have air holes arranged to allow air to reach the air holes on the battery cell.

64. An apparatus comprising:
a metal-air battery cell having a housing; and
means for applying external pressure to the cell housing.

65. The apparatus of claim 64, wherein the metal-air battery cell is a zinc-air battery cell.

66. The apparatus of claim 65, wherein the means for applying external pressure operates by pressing a first wall of the cell housing towards a second wall of the cell housing.

67. The apparatus of claim 65, wherein the cell housing is plastic.

68. The apparatus of claim 65, wherein the cell housing includes two substantially flat opposing plastic surfaces, and the means for applying external pressure presses the two surfaces towards each other.

69. The apparatus of claim 65, wherein the cell housing is metal.

70. The apparatus of claim 65, wherein the cell housing includes two substantially flat opposing metal surfaces, and the means for applying external pressure presses the two surfaces towards each other.

71. The apparatus of claim 65, wherein the means for applying external pressure applies between about 3.4 and about 5.2 N/cm^2 of pressure above atmospheric pressure.

72. The apparatus of claim 65, wherein the means for applying external pressure includes a strap that is tightened around the cell.

73. The apparatus of claim 72, wherein the strap is formed of an insulating material.

74. The apparatus of claim 65, wherein the means for applying external pressure includes blocks that are urged against the cell by at least one strap.

75. The apparatus of claim 74, wherein the battery cell has air holes, and the blocks have air holes arranged to allow air to reach the air holes on the battery cell.

76. The apparatus of claim 65, wherein the means for applying external pressure includes blocks that are urged against the cell housing by at least one spring.

77. The apparatus of claim 76, wherein the battery cell has air holes, and the blocks have air holes arranged to allow air to reach the air holes on the battery cell.

78. The apparatus of claim 65, wherein the means for applying external pressure includes a heavy object that is placed on top of the cell.

79. The apparatus of claim 65, wherein the means for applying external pressure includes two blocks that are urged together using at least one screw.

80. The apparatus of claim 79, wherein the battery cell has air holes, and the blocks have air holes arranged to allow air to reach the air holes on the battery cell.

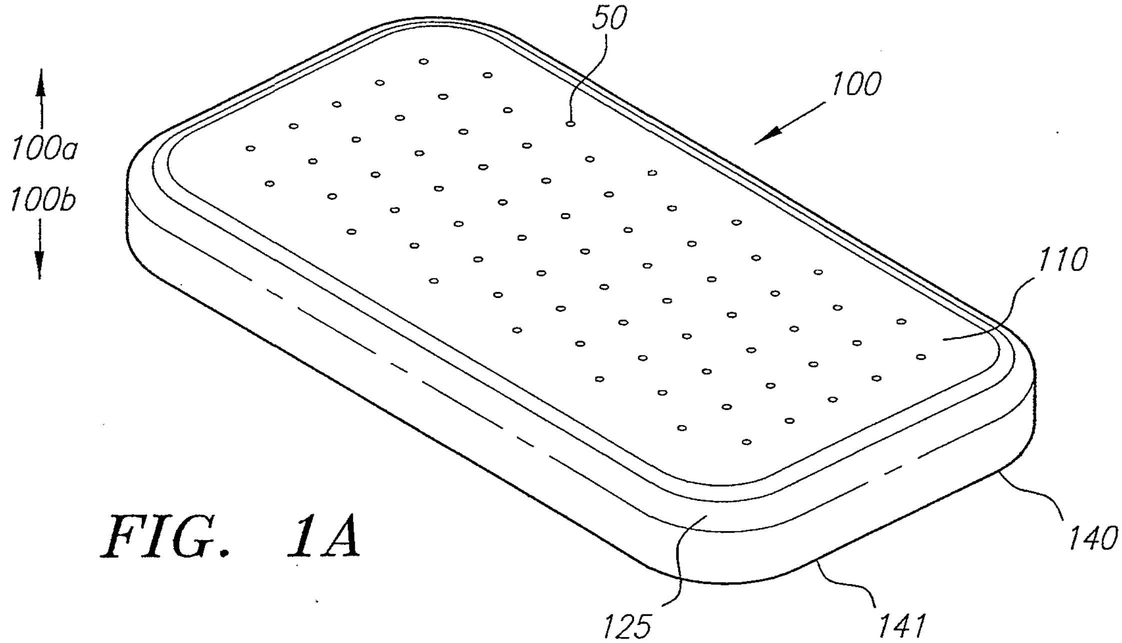

FIG. 1A

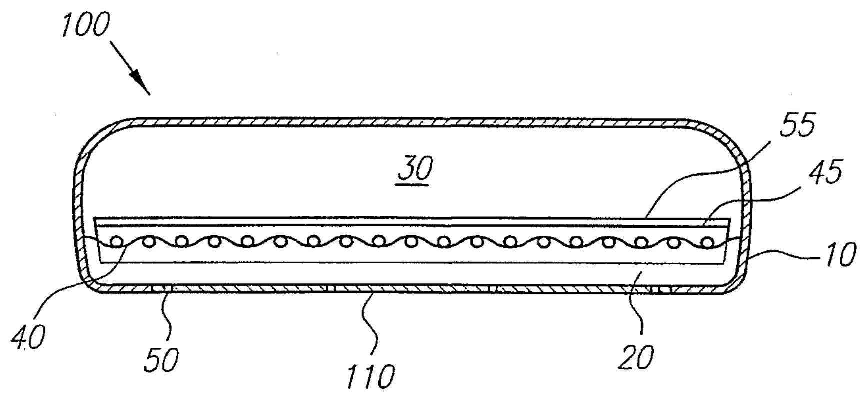

FIG. 1B

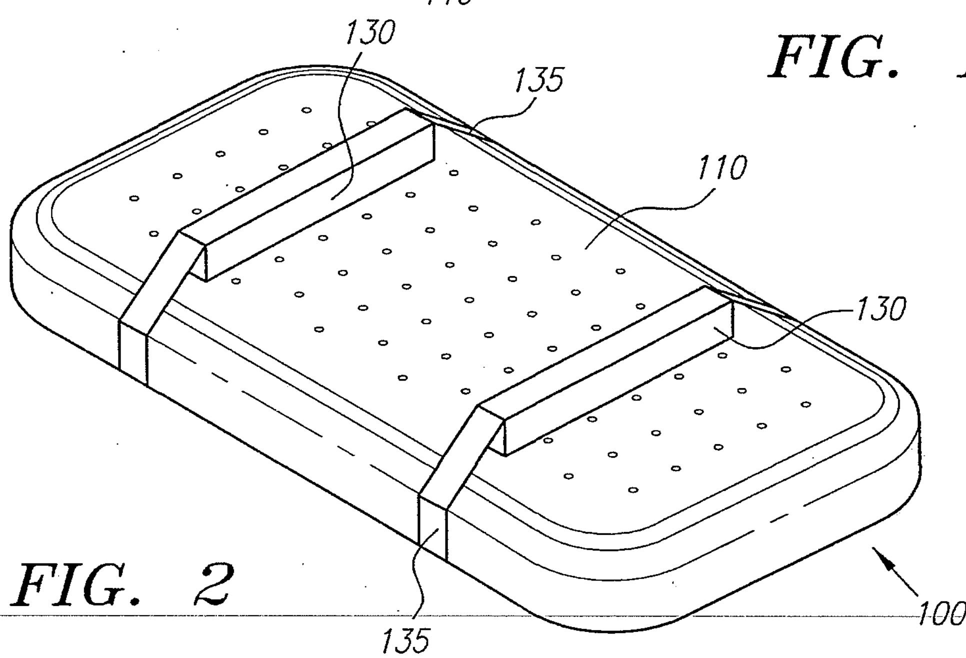

FIG. 2

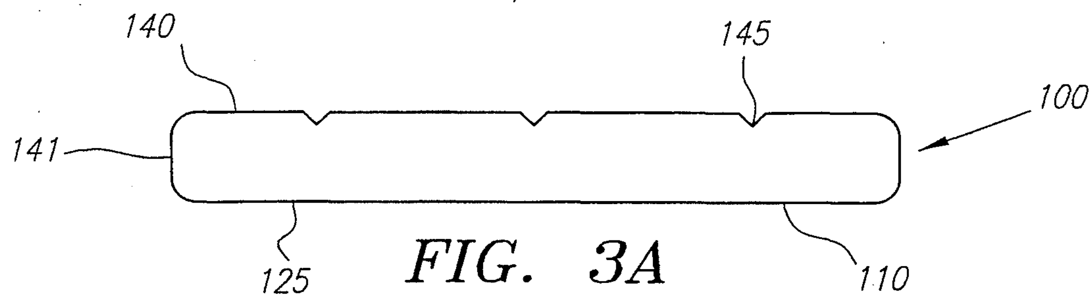

FIG. 3A

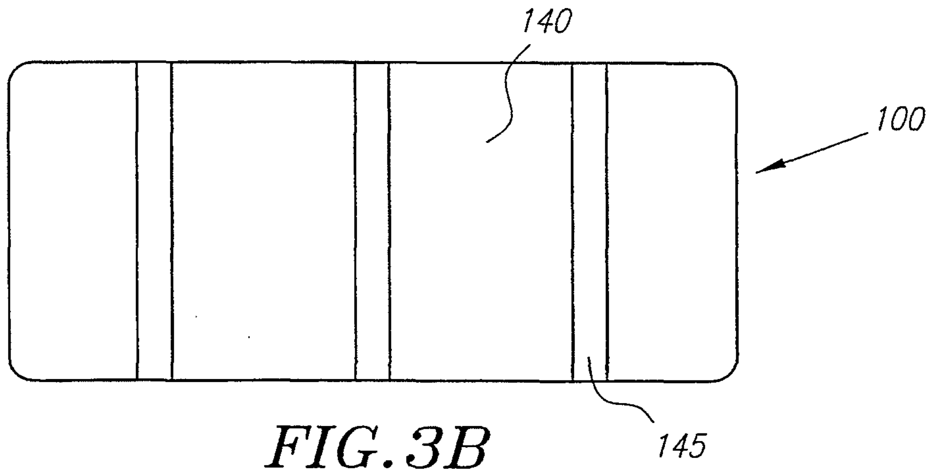

FIG.3B

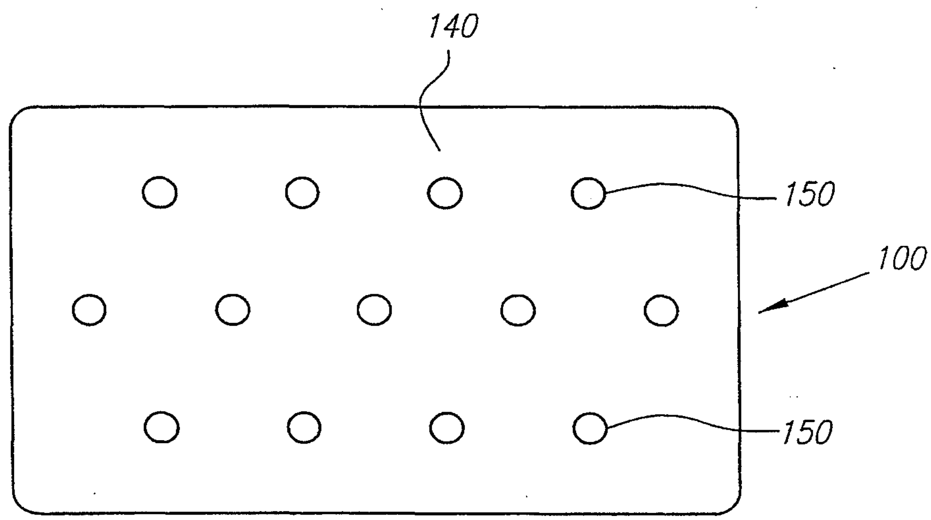

FIG. 3C

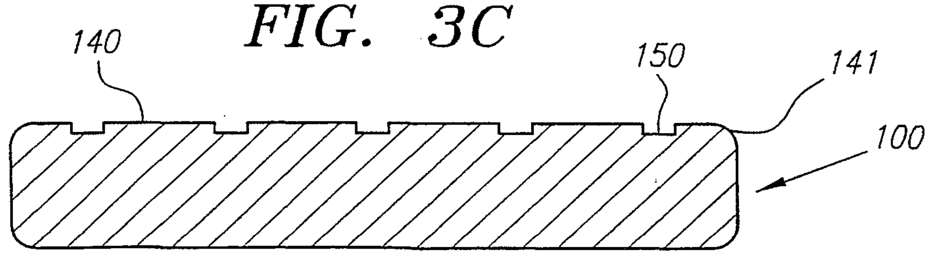

FIG. 3D

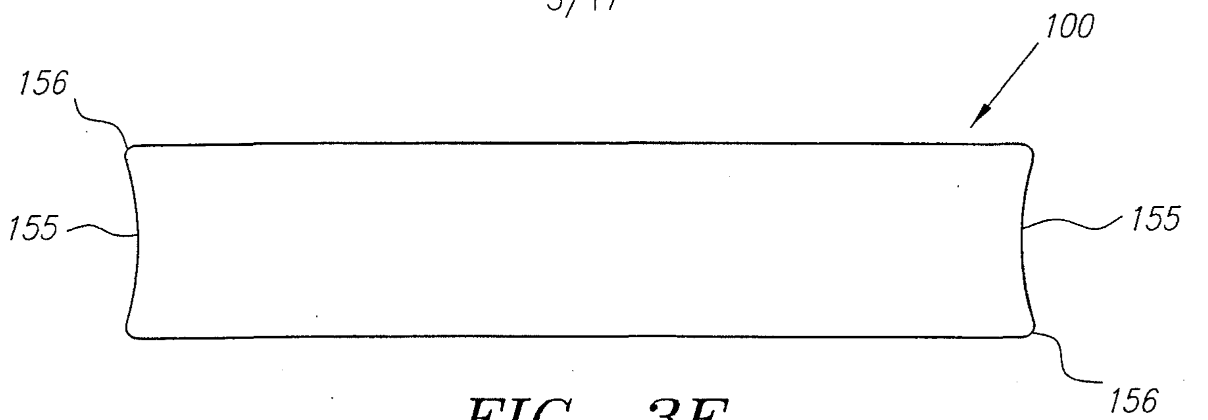

FIG. 3E

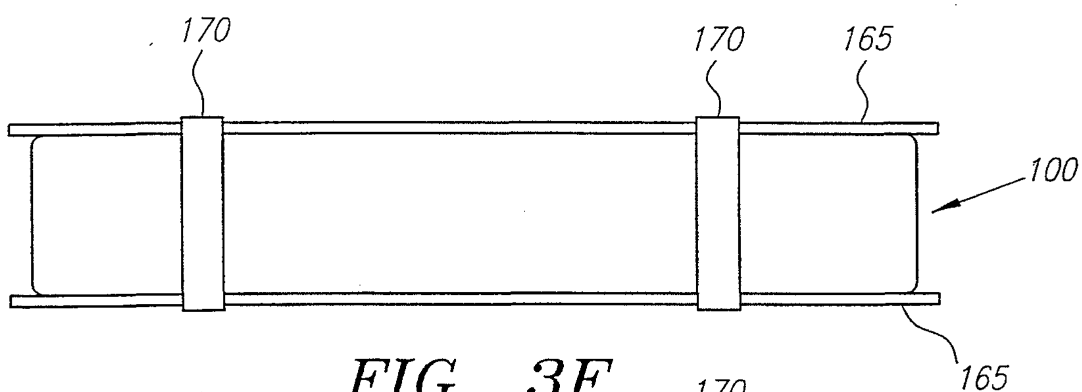

FIG. 3F

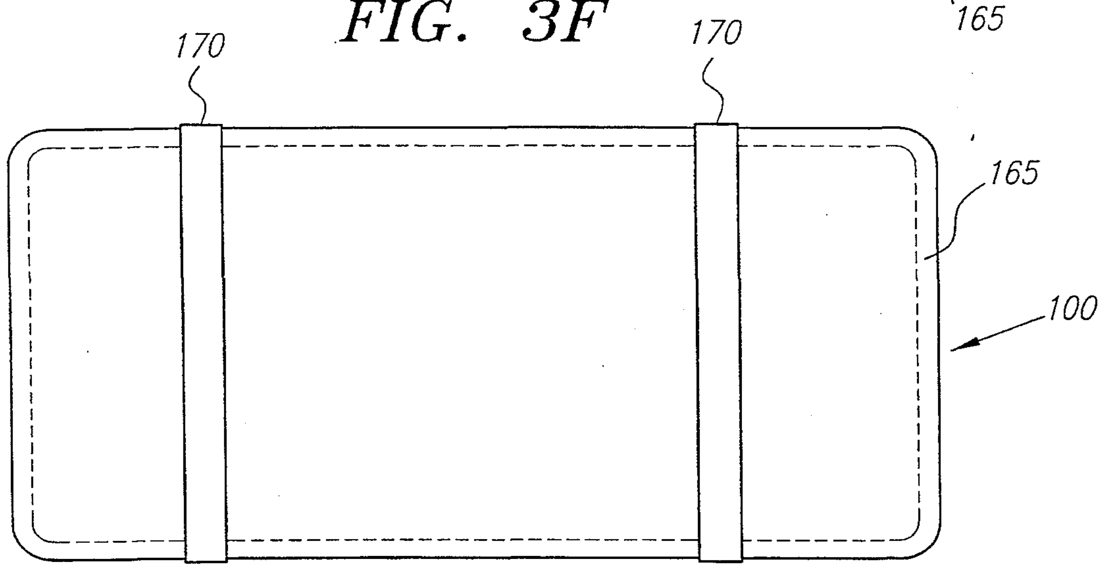

FIG. 3G

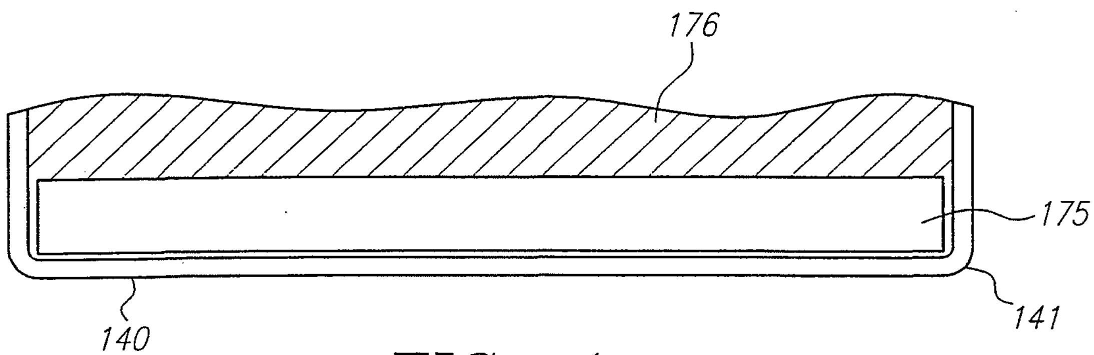

FIG. 4

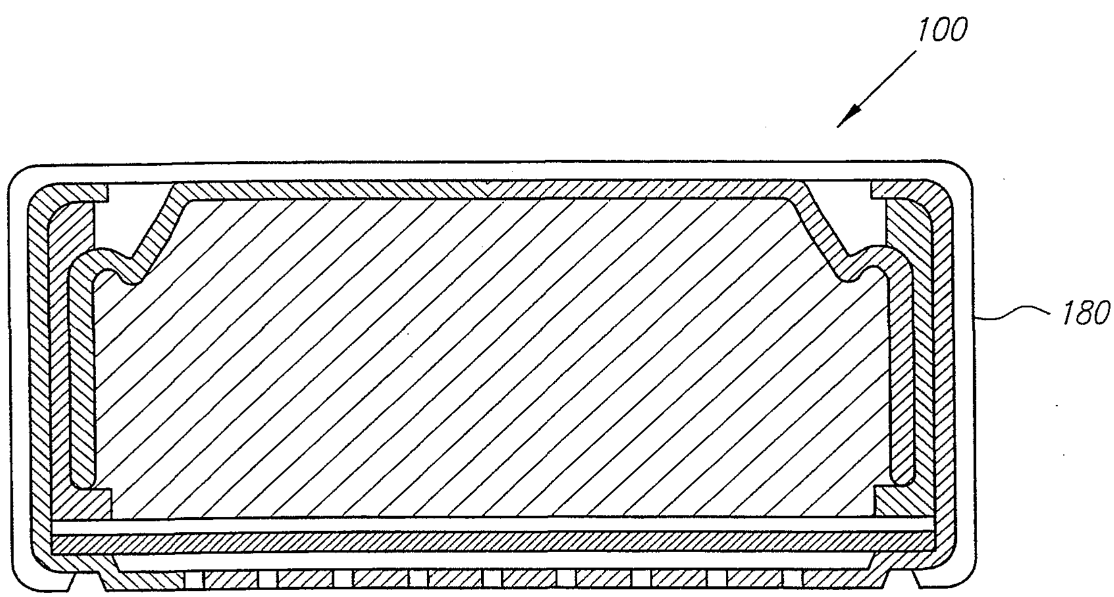

FIG. 5

TYPICAL CURVE OF VOLTAGE DELAY PHENOMENA (LOW AND HIGH CURRENT) IN CB: (REV0, y2532 AT 30% DISCHARGE)

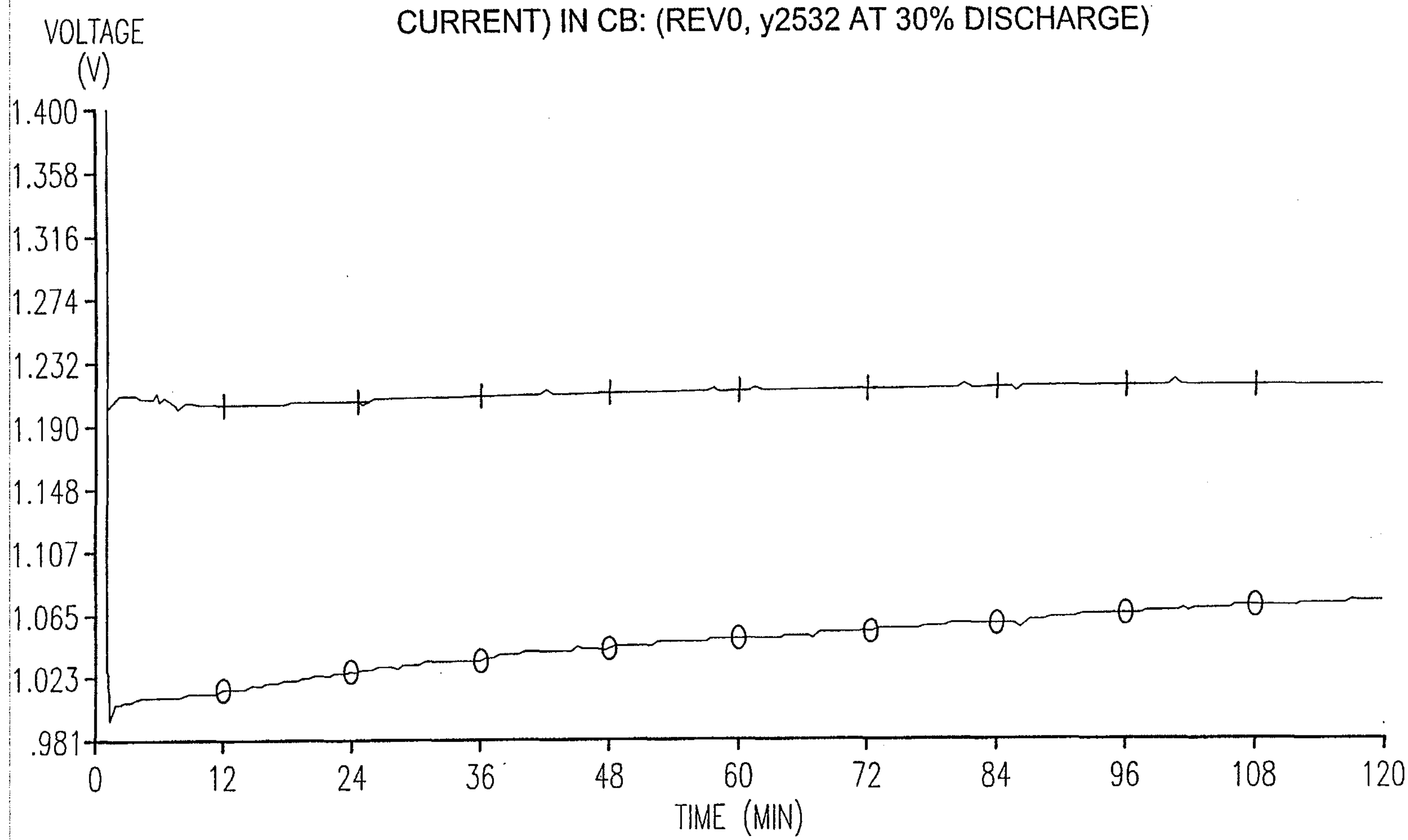

FIG. 6

□ = y2532gd4.005 NON PULSING
0 = y2532gd4.005 PULSE HI
+ = y2532gd4.005 PULSE LOW

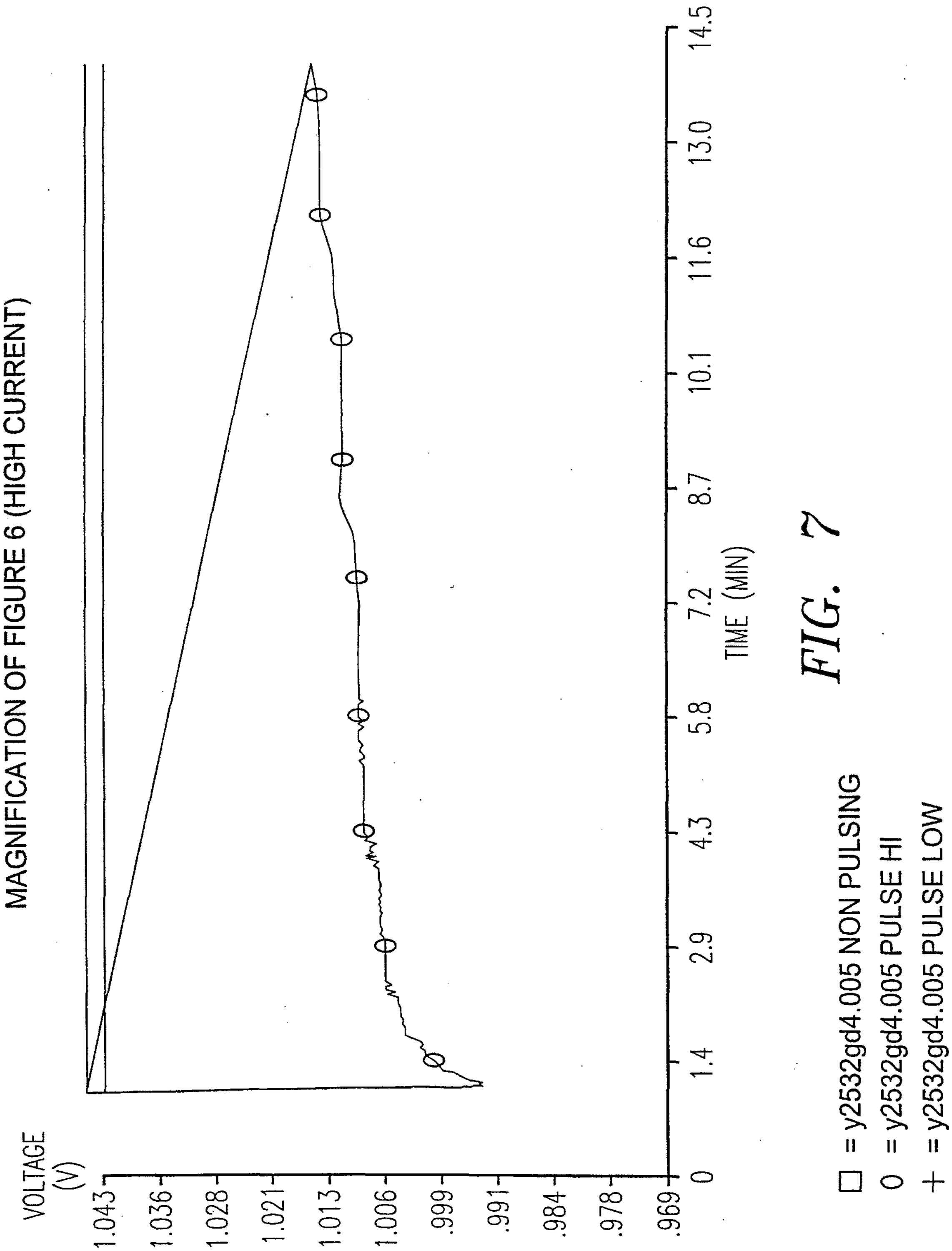
MAGNIFICATION OF FIGURE 6 (HIGH CURRENT)
VOLTAGE (V)
1.043
1.036
1.028
1.021
1.013
1.006
.999
.991
.984
.978
.969
0
1.4
2.9
4.3
5.8
7.2
8.7
10.1
11.6
13.0
14.5
TIME (MIN)
□ = y2532gd4.005 NON PULSING
O = y2532gd4.005 PULSE HI
+ = y2532gd4.005 PULSE LOW

FIG. 7

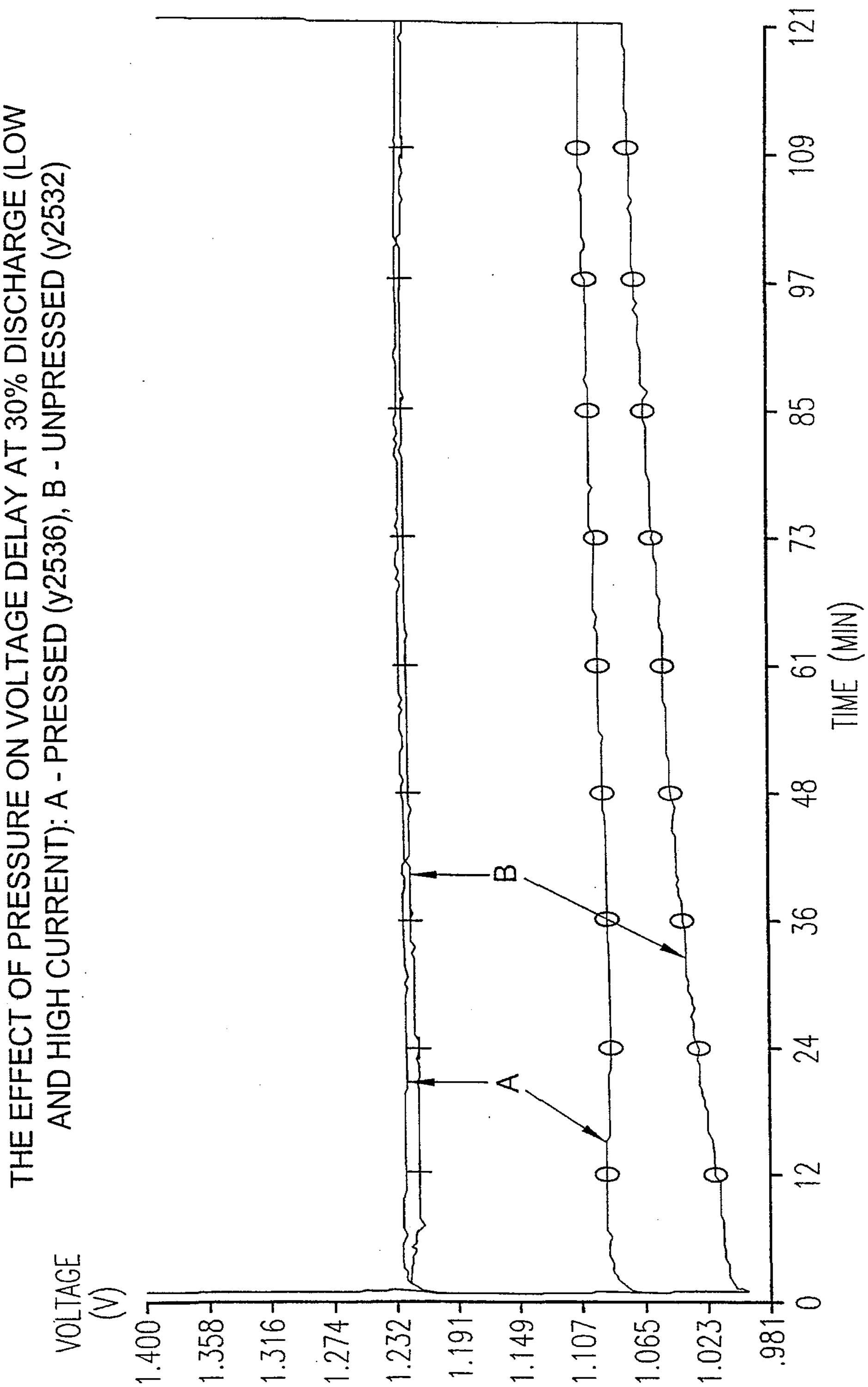

FIG. 8

□ = y2536gd4.001 NON PULSING
O = y2536gd4.001 PULSE HI
+ = y2536gd4.001 PULSE LOW

MAGNIFICATION OF FIGURE 8(HIGH CURRENT)

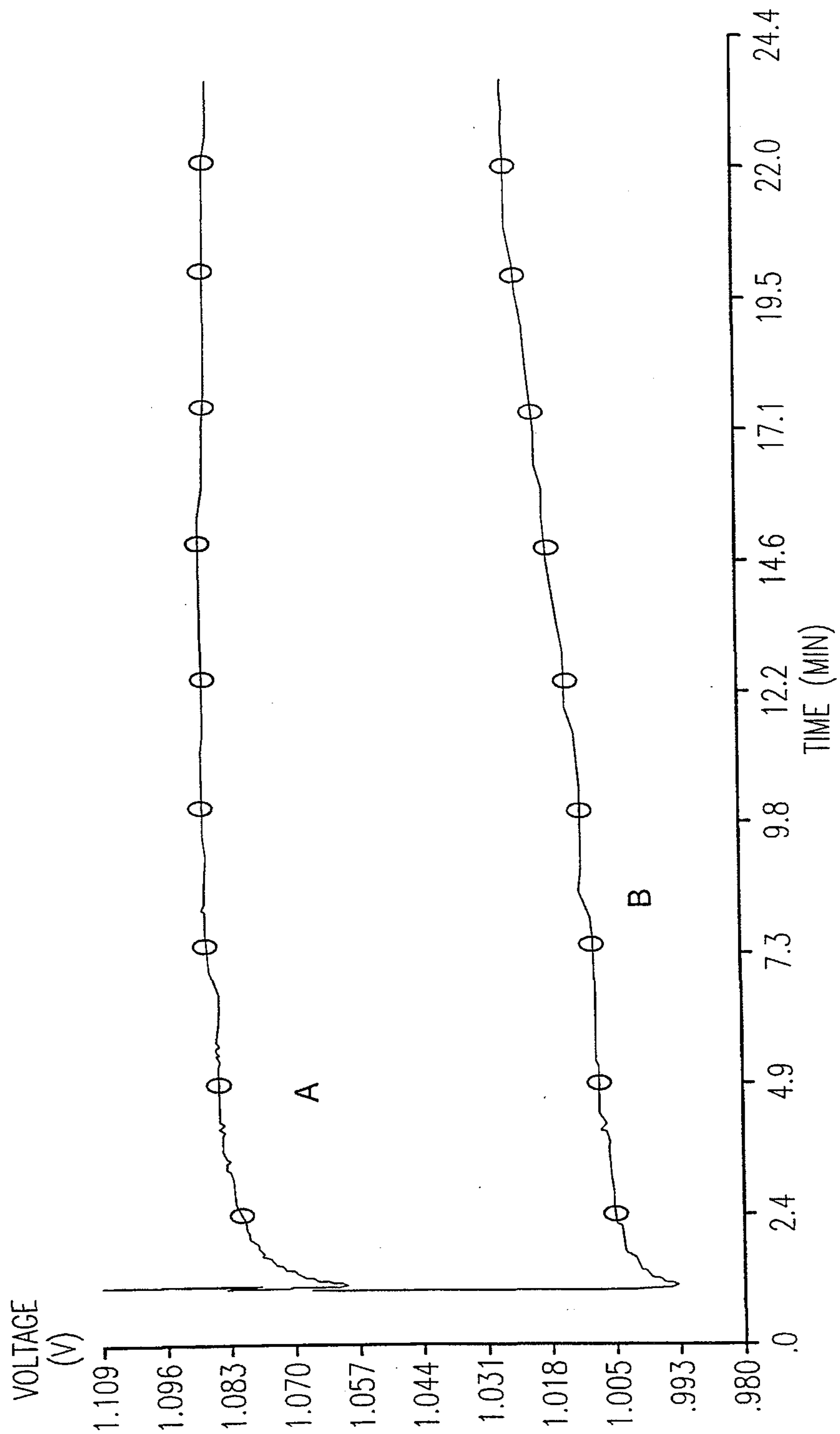

FIG. 9

□ = y2536gd4.001 NON PULSING
O = y2536gd4.001 PULSE HI
+ = y2536gd4.001 PULSE LOW

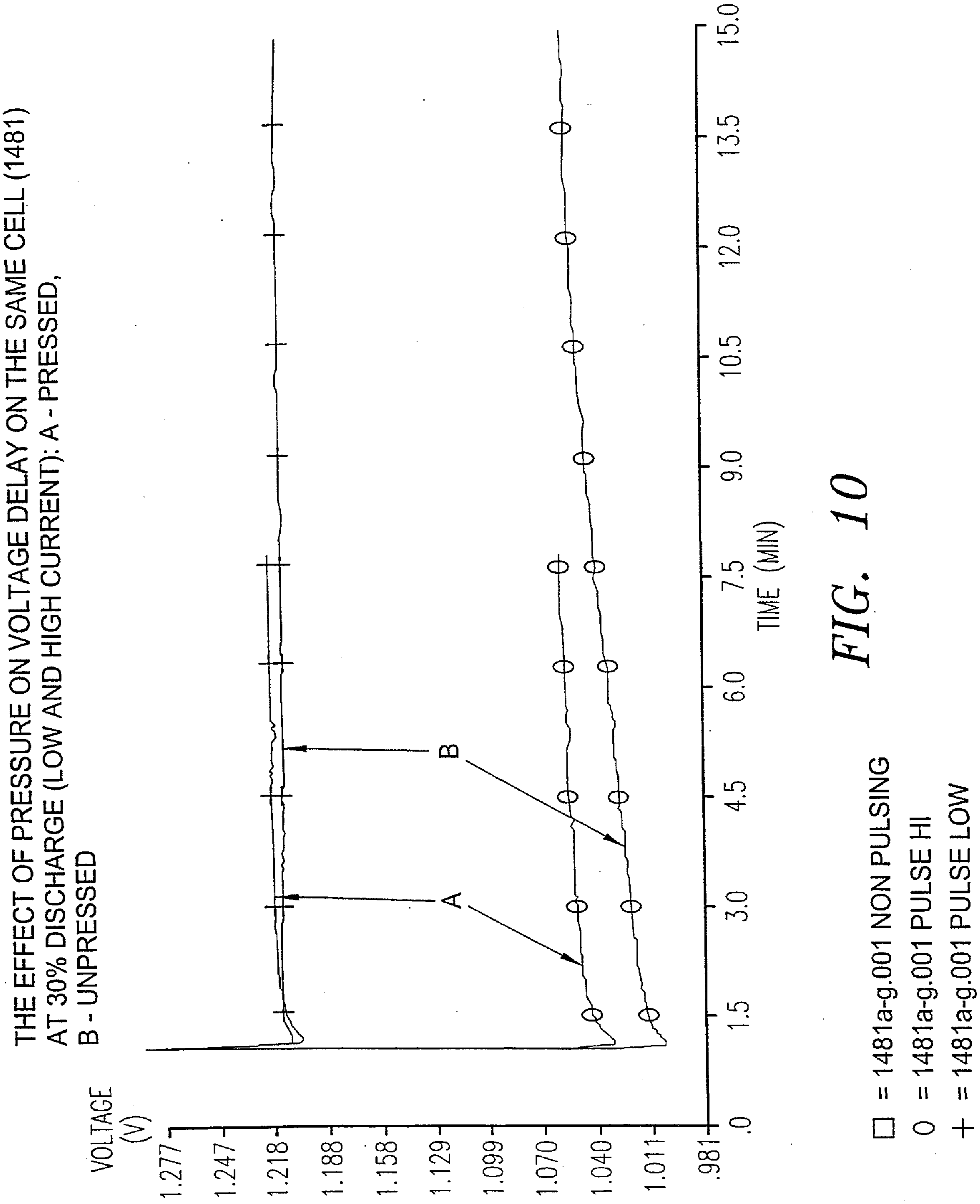
THE EFFECT OF PRESSURE ON VOLTAGE DELAY ON THE SAME CELL (1481)
AT 30% DISCHARGE (LOW AND HIGH CURRENT): A - PRESSED,
B - UNPRESSED
VOLTAGE (V)
1.277
1.247
1.218
1.188
1.158
1.129
1.099
1.070
1.040
1.011
.981
.0
1.5
3.0
4.5
6.0
7.5
9.0
10.5
12.0
13.5
15.0
TIME (MIN)
A
B
□ = 1481a-g.001 NON PULSING
O = 1481a-g.001 PULSE HI
+ = 1481a-g.001 PULSE LOW

FIG. 10

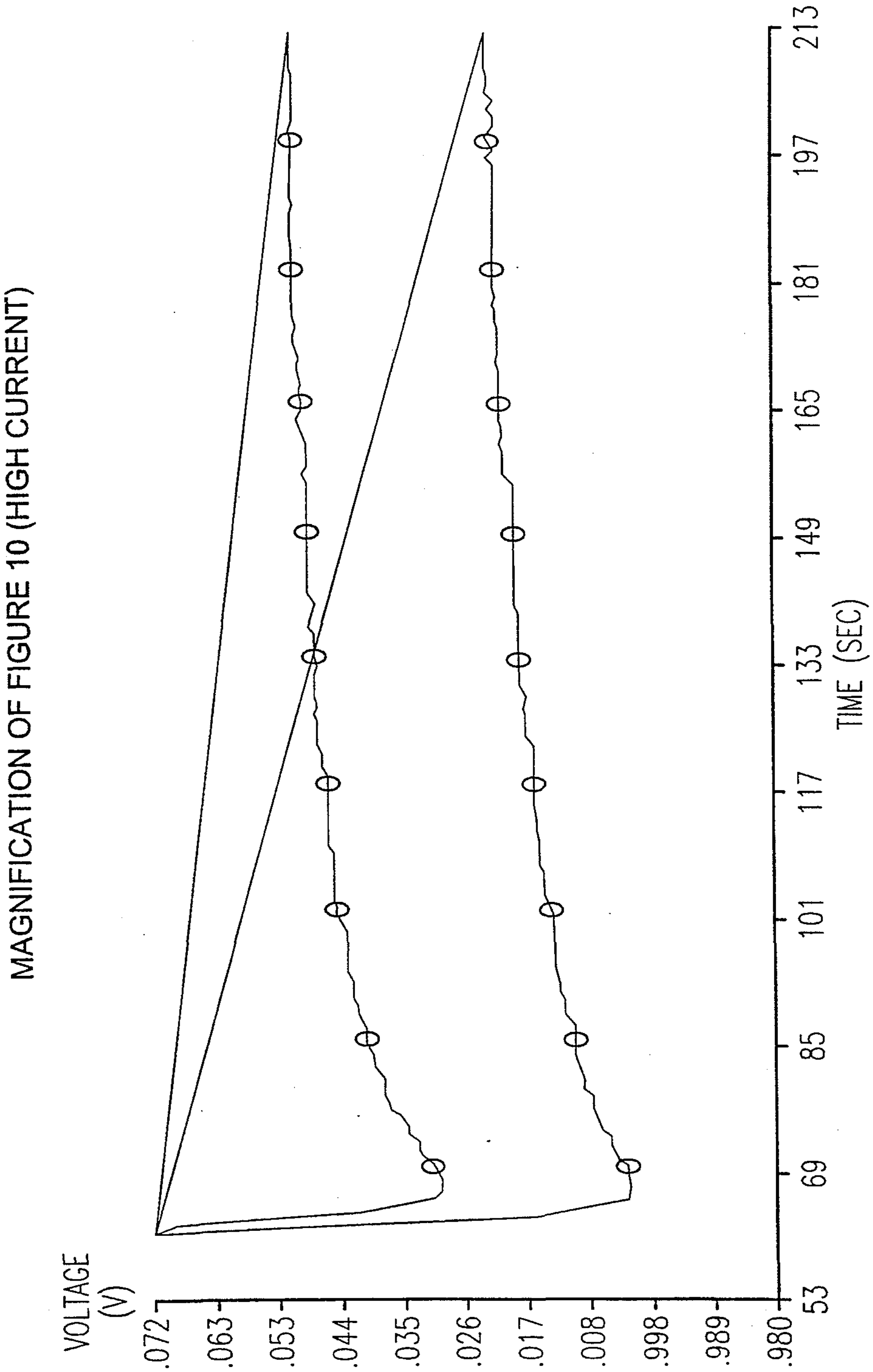

FIG. 11

□ = 1481a-g.001 NON PULSING
0 = 1481a-g.001 PULSE HI
+ = 1481a-g.001 PULSE LOW

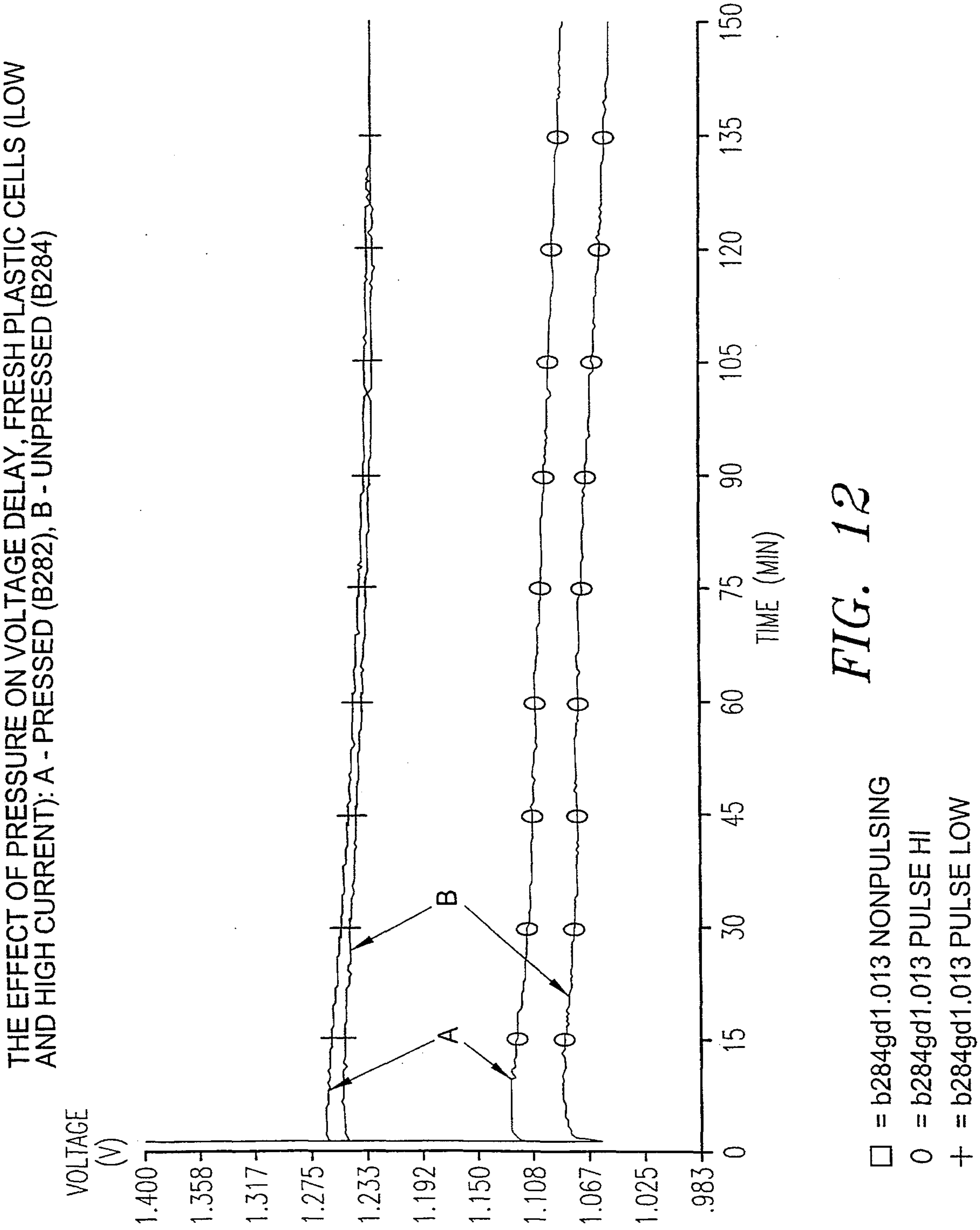
THE EFFECT OF PRESSURE ON VOLTAGE DELAY, FRESH PLASTIC CELLS (LOW AND HIGH CURRENT): A - PRESSED (B282), B - UNPRESSED (B284)
VOLTAGE (V)
1.400
1.358
1.317
1.275
1.233
1.192
1.150
1.108
1.067
1.025
.983
TIME (MIN)
0
15
30
45
60
75
90
105
120
135
150
A
B
□ = b284gd1.013 NONPULSING
O = b284gd1.013 PULSE HI
+ = b284gd1.013 PULSE LOW

FIG. 12

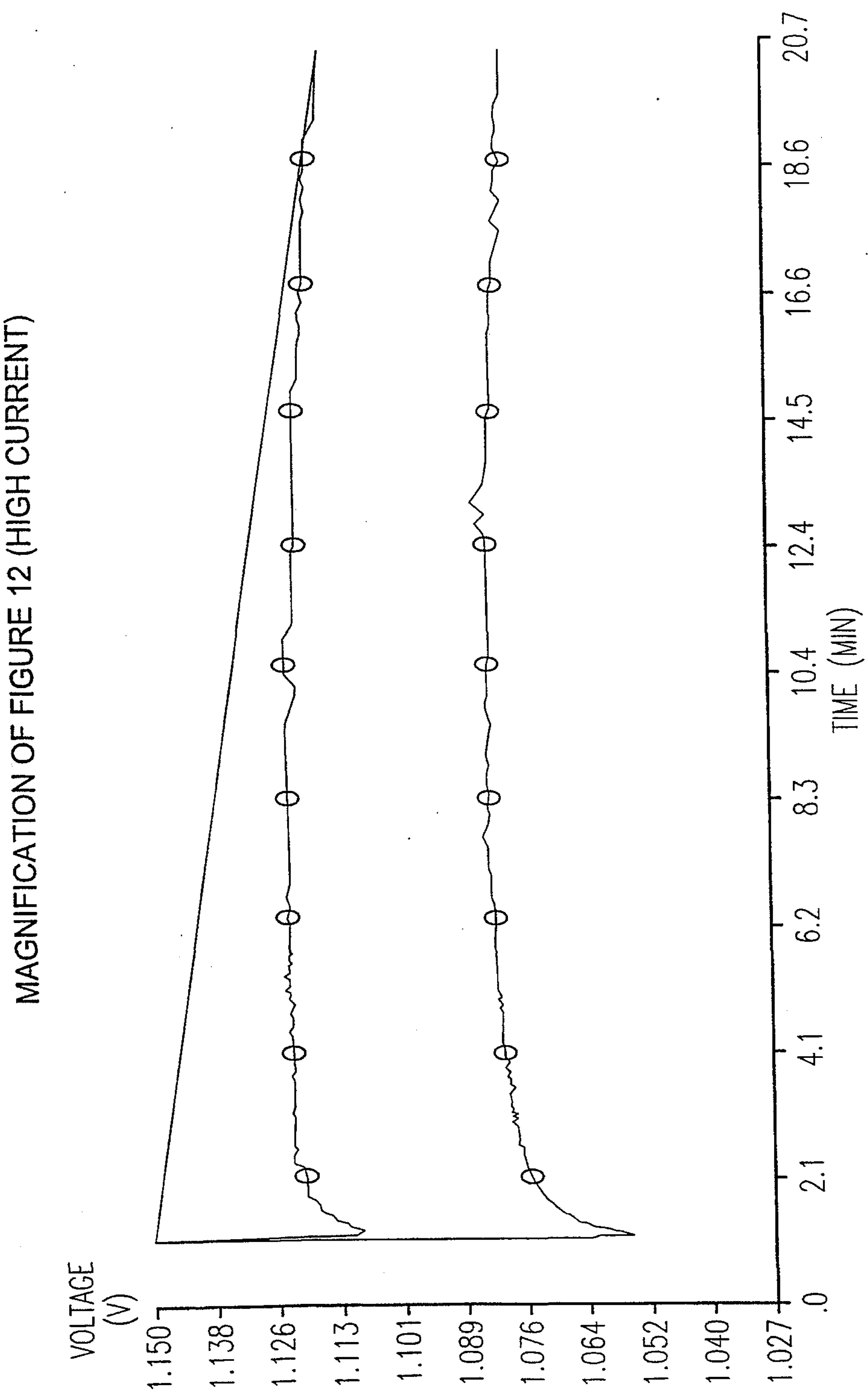

FIG. 13

□ = b284gd1.013 NONPULSING
O = b284gd1.013 PULSE HI
+ = b284gd1.013 PULSE LOW

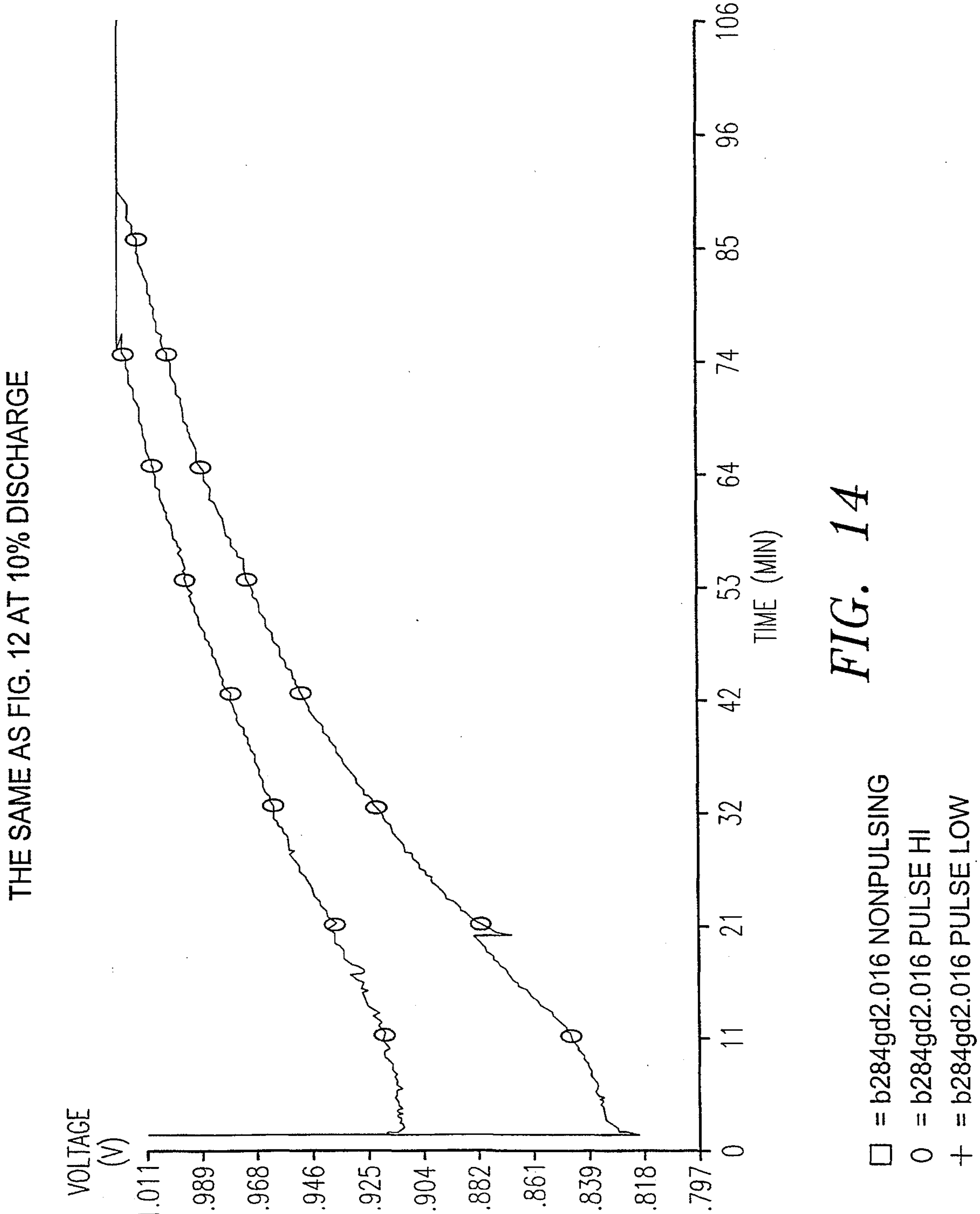
THE SAME AS FIG. 12 AT 10% DISCHARGE
VOLTAGE (V)
1.011
.989
.968
.946
.925
.904
.882
.861
.839
.818
.797
TIME (MIN)
0
11
21
32
42
53
64
74
85
96
106
□ = b284gd2.016 NONPULSING
O = b284gd2.016 PULSE HI
+ = b284gd2.016 PULSE LOW

FIG. 14

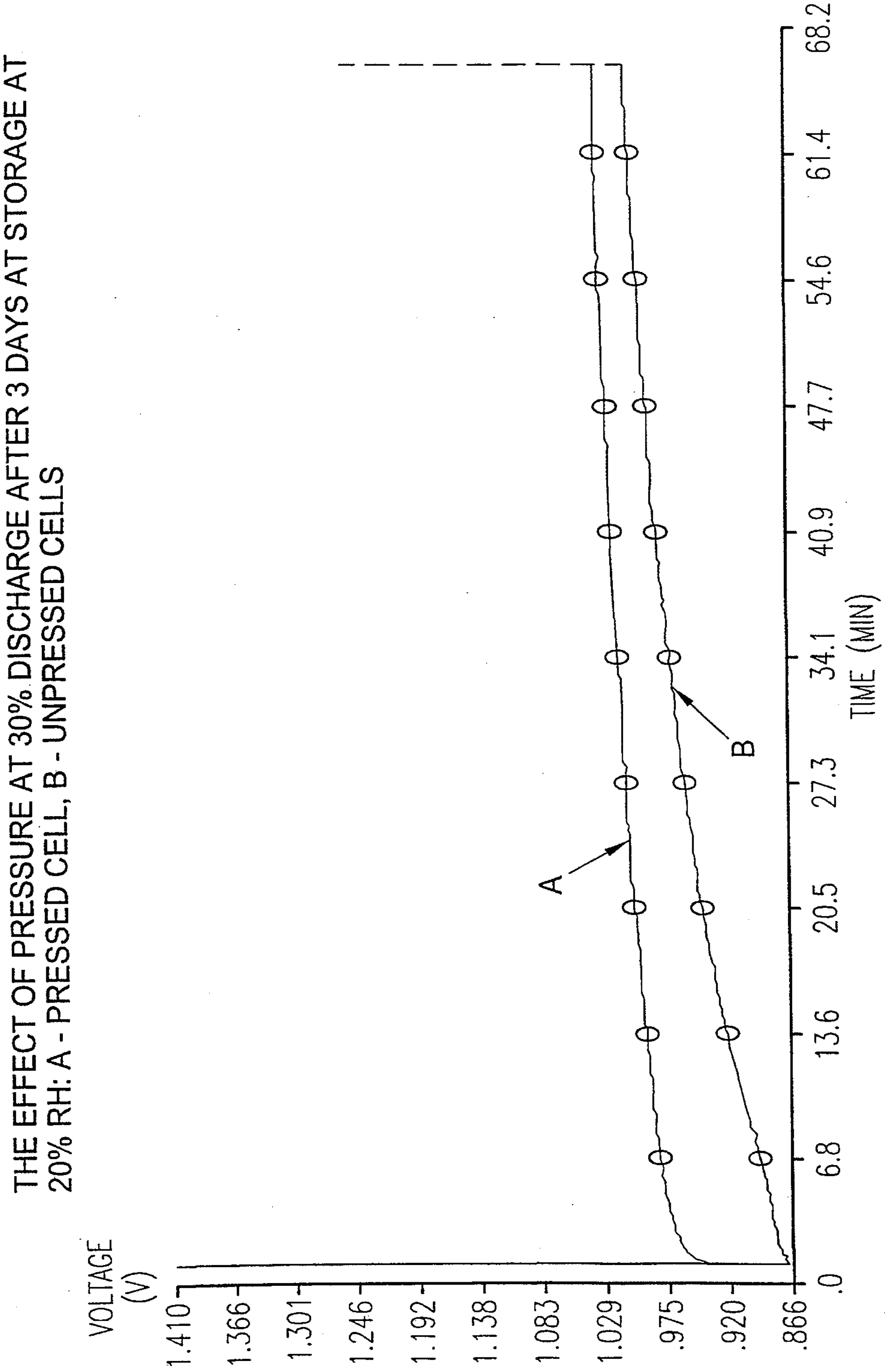

FIG. 15

□ = y4957-g2.020 NONPULSING
O = y4957-g2.020 PULSE HI

MAGNIFICATION OF FIGURE 15

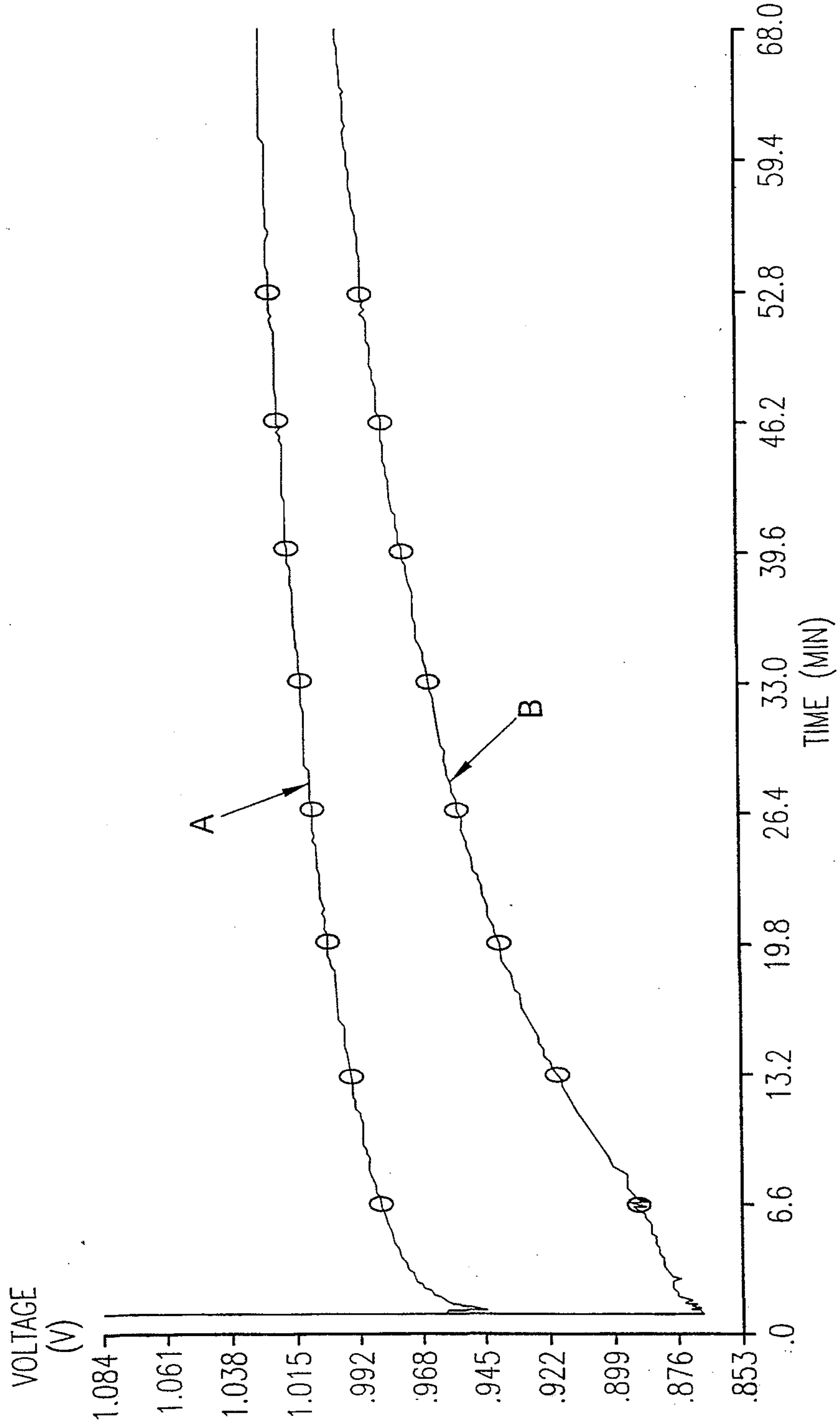

FIG. 16

□ = y4957-g2.020 NONPULSING
O = y4957-g2.020 PULSE HI

THE EFFECT OF PRESSURE ON PERFORMANCE (GSM -0 CELSIUS CENTIGRADE)

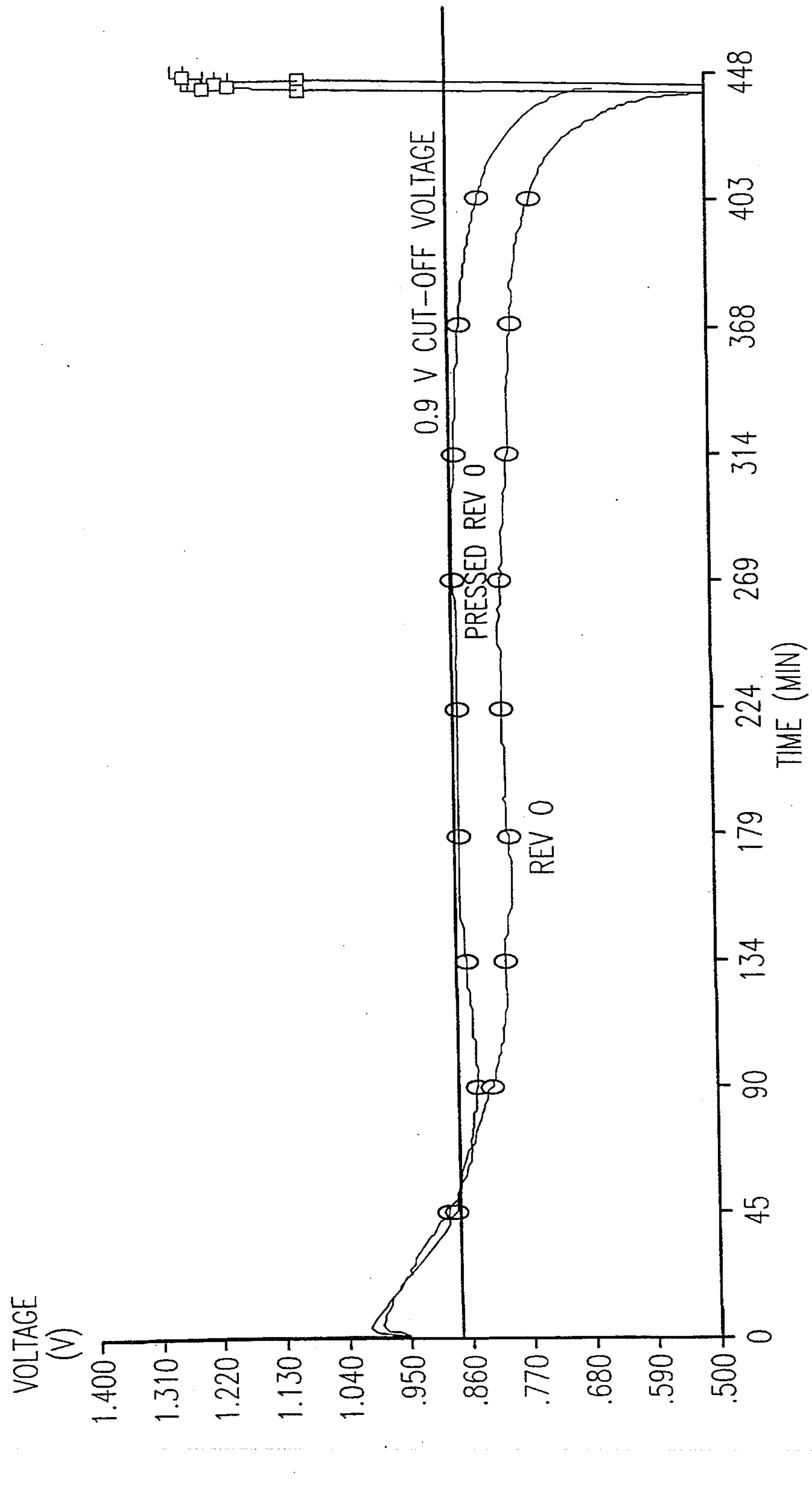

FIG. 17

□ = y5782-g.032 NON PULSING
0 = y5782-g.032 PULSE HI

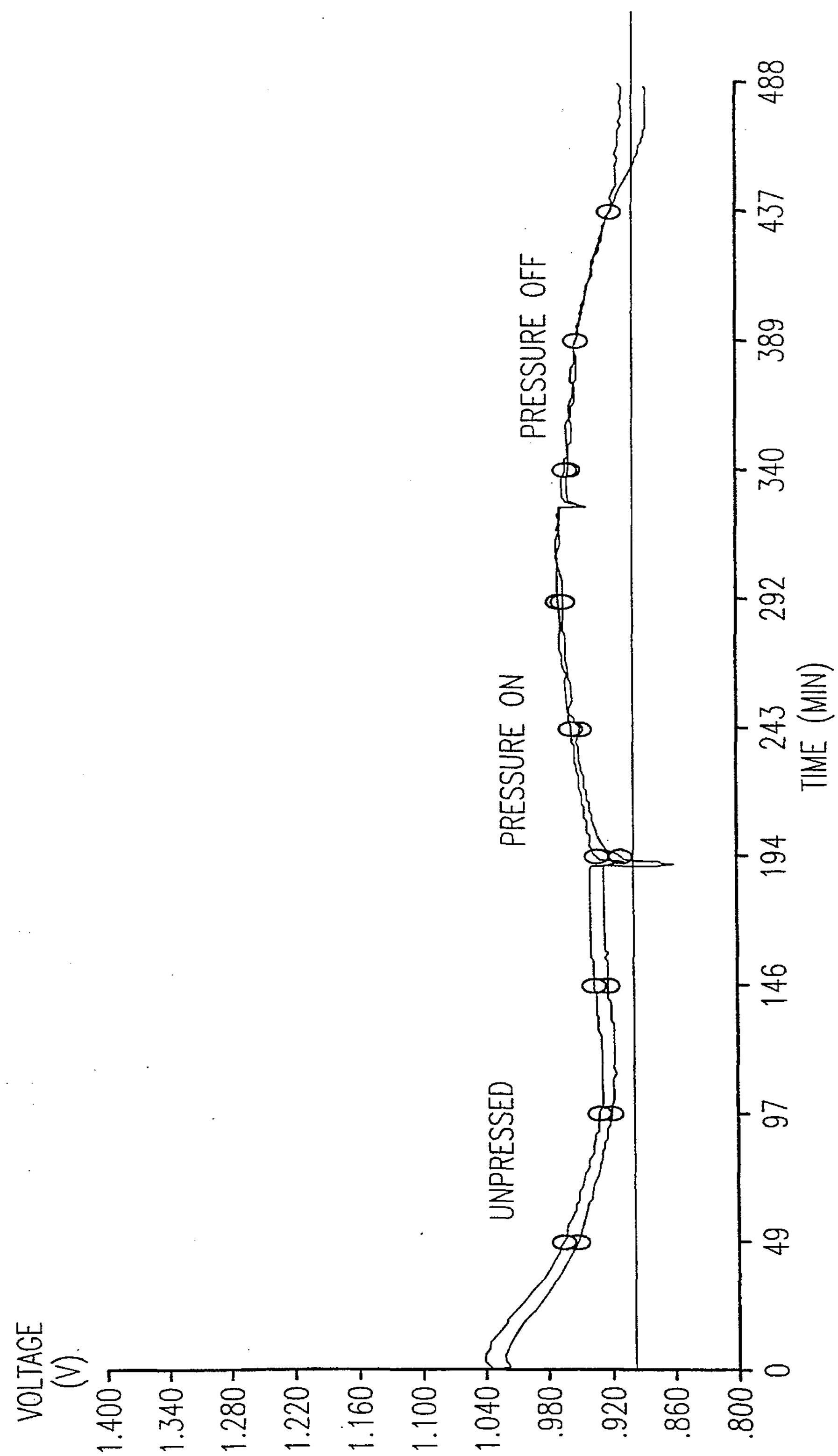
VOLTAGE (V)
1.400
1.340
1.280
1.220
1.160
1.100
1.040
.980
.920
.860
.800
0
49
97
146
194
243
292
340
389
437
488
TIME (MIN)
UNPRESSED
PRESSURE ON
PRESSURE OFF
□ = y7051-g.032 NON PULSING
O = y7051-g.032 PULSE HI

FIG. 18

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/28120

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M12/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 08358 A (VOLTEK INC., BELLEVILLE, US) 14 April 1994 (1994-04-14) page 1, line 3 - line 5 page 1, line 23 - line 26 page 13, line 3 -page 15, line 13 figures 6,21	1,4,31, 64
A		34-36, 70,72, 73,76
X	US 4 262 062 A (ZATSKY NORMAN, SOUTHBURY, CONN., US) 14 April 1981 (1981-04-14) column 2, line 58 -column 4, line 46 figures 1-4	64-66, 68,70

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 March 2000	05/04/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Peis, S

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/US 99/28120

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